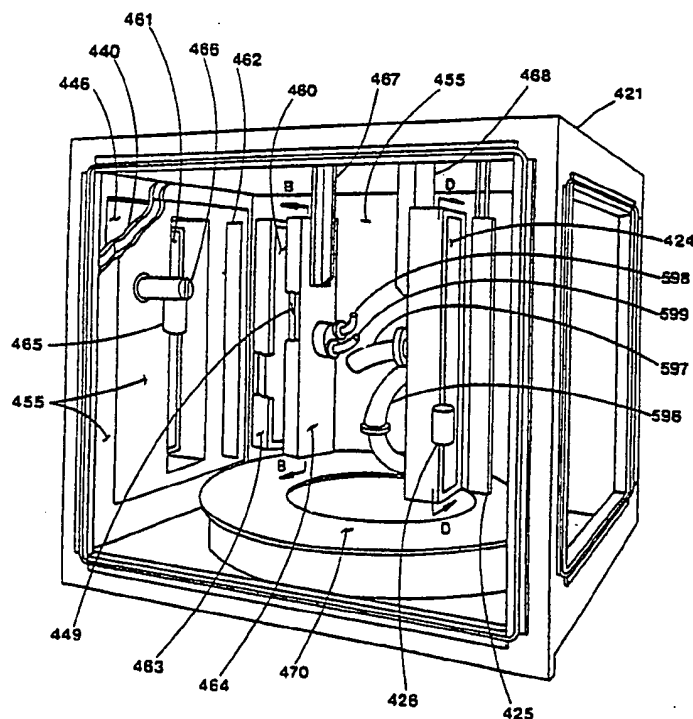


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(54) Title: PHYSICAL VAPOR DEPOSITION DUAL COATING APPARATUS AND PROCESS



(57) Abstract

A machine for covering a substrate (Fig. 14, 540) by means of both cathodic arc plasma deposition (CAPD) (Fig. 2) and magnetron sputtering (Fig. 1) without breaking vacuum in a single chamber (Fig. 14, 421). A computer system monitors (Fig. 3, 403, 405) and controls all coating process parameters to coat in any sequence multiple thin film layers using either the CAPD or magnetron sputtering process. A rotating substrate table (Fig. 14, 470) used in conjunction with internal and external targets coats both sides of the substrate simultaneously.

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PHYSICAL VAPOR DEPOSITION DUAL COATING
APPARATUS AND PROCESS

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FIELD OF THE INVENTION

10 The present invention relates to vacuum coating
production system utilizing both cathodic arc emission
and magnetron sputtering processes.

BACKGROUND OF THE INVENTION

Sputtering Processes.

15 Over the past 30 years or so there have been
numerous reviews of sputtering and sputtering processes
for film deposition.

20 Because there are so many interactions among
parameters in sputtering systems, it is impossible to
separate them completely.

25 Typically, the target (a plate of the material
to be deposited or the material from which a film is to
be synthesized) is connected to a negative DC voltage
supply (or an RF power supply). The substrate is the
material to be coated and it faces the target. The
substrate may be grounded, floating, biased, heated,
cooled, or some combination of these. A gas is
introduced to provide a medium in which a glow discharge
can be initiated and maintained. Gas pressures ranging
30 from a few millitorr to several tens of millitorr are
used. The most common sputtering gas is argon.

35 When the glow discharge is started, positive
ions strike the target plate and remove mainly neutral
target atoms by momentum transfer, and these condense on
the substrate to form thin films. There are, in
addition, other particles and radiation produced at the
target, all of which may affect film properties
(secondary electrons and ions, desorbed gases, x-rays,
and photons). The electrons and negative ions are
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5 accelerated toward the substrate platform and bombard it
and the growing film. In some instances, a bias
potential (usually negative) is applied to the substrate
holder, so that the growing film is subject to positive
ion bombardment. This is known variously as bias
sputtering or ion plating.

10 In some cases, gases or gas mixtures other than
Ar are used. Usually this involves some sort of reactive
sputtering process in which a compound is synthesized by
sputtering a metal target (e.g., Ti) in a reactive gas
(e.g., O₂ or Ar-O₂ mixtures) to form a compound of the
15 metal and the reactive gas species (e.g., TiO₂).

Emission of Neutral Particles-The Sputtering Yield.

The sputtering yield is defined as the number of
atoms ejected from a target surface per incident ion. It
20 is the most fundamental parameter of sputtering
processes. Yet all of the surface interaction phenomena
involved that contribute to the yield of a given surface
are not completely understood. Despite this, an
impressive body of literature exists showing the yield to
25 be related to momentum transfer from energetic particles
to target surface atoms.

It is estimated that 1% of the energy incident
on a target surface goes into ejection of sputtered
particles, 75% into heating of the target and the
30 remainder is dissipated by secondary electrons that
bombard and heat the substrates. An improved process
called magnetron sputtering uses magnetic fields to
conduct electrons away from the substrate surface thereby
reducing the heat.

35 There are three basic effects that occur at a
substrate during glow discharge sputtering: (1)
condensation of energetic vapor, (2) heating, and (3)
bombardment by a variety of energetic species. The sum

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5 of all of these effects must be carefully controlled,
and, since they are all interdependent, this is sometimes
difficult.

For a given target material both deposition rate
and uniformity are influenced by system geometry, target
voltage, sputtering gas, gas pressure, and power. All
10 other things being equal, rates are linearly proportional
to power and decrease with increasing target-substrate
separation. The sputtering gas influences deposition
rate in the same way as it affects sputtering yields. As
the gas pressure is increased the discharge current
15 increases (increasing rate), but return of material to
the target by backscattering also increases (decreasing
rate). This is further complicated in some cases by
increased Penning ionization at higher pressures which
increases the rate by self-sputtering. The sum of all of
20 this leads to gas pressure or a small range of gas
pressure at which the rate is a maximum, and this must be
determined empirically for each application. The optimum
pressure may be anywhere between a few mTorr and several
tens of mTorr.

25 In general, for a given gas pressure there will
be an optimum target-substrate separation to produce the
best uniformity. For small targets (15-cm diameter) this
separation is generally small (a few centimeters), while
for larger targets, the optimum separation may be
30 considerably larger (10-20 cm).

Unquestionably, the hallmark of the sputtering
processes described is versatility, both in terms of
materials that can be deposited and process parameters
that can be adjusted to tailor the properties of thin
35 films as desired. However, the sheer number of critical
process parameters and their complex interrelationships
can often make these processes difficult to control. In
general, these processes are found to be most useful in
applications requiring rather thin films (generally 1
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micron because of relatively low deposition rates) and/or in cases where the desired material simply cannot be deposited stoichiometrically any other way.

The above portion of this patent application was reprinted with permission from the publishers of Thin Film Processes, edited by John L. Vossen and Werner Kern (copyright Academic Press, Inc., New York, 1978, pp. 12-62).

Cathodic Arc Plasma Deposition.

In the past ten years major advancements have been made in a related physical deposition process called cathodic arc plasma deposition (CAPD).

In the CAPD process target material is evaporated by the action of vacuum arcs. The target source material is the cathode in the arc circuit. The basic components of a CAPD system consist of a vacuum chamber, a cathode and an arc power supply, a means of igniting an arc on the cathode surface, an anode, a substrate and a substrate bias power supply. Arcs are sustained by voltages typically in the range of 15 - 50 V, depending on the target cathodic material employed. Typical arc currents in the range of 30 - 400 A are employed. Arcing is initiated by the application of a high voltage pulse to an electrode placed near the cathode (gas discharge ignition) and/or by mechanical ignition. The evaporation occurs as a result of the cathodic arc spots which move randomly on the surface of the cathode at speeds typically of the order of 10^2 m/s. The arc spot motion can also be controlled with the help of appropriate confinement boundaries and/or magnetic fields. The arc spots are sustained owing to material plasma generated with the arc itself. The target cathodic material can be a metal, a semiconductor or an insulator.

5 The CAPD process is a unique process and is
markedly different from other physical vapor deposition
(PVD) processes. Some of the characteristic features of
the CAPD process are as follows.

- (i) The core of the CAPD process is the arc
spot which generates material plasma.
- 10 (ii) A high percentage (30% - 100%) of the
material evaporated from the cathode surface is ionized.
- (iii) The ions exist in multiple charge states in
the plasma, e.g. Ti, Ti^+ , Ti^{+2} and Ti^{+3} etc.
- 15 (iv) The kinetic energies of the ions are
typically in the range 10-100 eV.

These features result in deposits that are of
superior quality compared with those from other physical
vapor deposition processes. Some of these advantages are
as follows.

- 20 (a) Good quality films over a wide range of
deposition conditions, e.g. stoichiometric compound films
with superior adhesion and high density, can be obtained
over a wide range of reactive gas pressure and
metal/refractory evaporation rates.
- 25 (b) High deposition rates for metals, alloys
and compounds with excellent coating uniformity.
- (c) Low substrate temperatures.
- (d) Retention of alloy composition from source
to deposits.
- 30 (e) Ease in deposition of compound films.

Cathodic Arc Emission Characteristics.

35 The cathodic arc results in a plasma discharge
within the material vapor released from the cathode
surface. The arc spot is typically a few micrometers in
size and carries current densities as high as 10 amps per
square micrometer. This high current density causes
flash evaporation of the source material and the
resulting evaporant consists of electrons, ions, neutral

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5 vapor atoms and microdroplets. The electrons are
accelerated toward the cloud of positive ions. The
emissions from the cathode spots are relatively constant
over a wide range of arc current as the cathode spots
split into a number of spots. The average current
10 carried per spot depends on the nature of the cathode
material.

It is likely that almost 100% of the material
may be ionized within the cathode spot region. These
ions are ejected in a direction almost perpendicular to
the cathode surface. The microdroplets, however, have
15 been postulated to leave the cathode surface at angles up
to about 30° above the cathode plane. The microdroplet
emission is a result of extreme temperatures and forces
that are present within emission craters.

The cathodic arc plasma deposition process was
20 considered unsuitable for decorative applications until
recently, due to the presence of microdroplets in the
film.

Latest developments involving elimination of
microdroplets in the CAPD process has provided a
25 significant alternative to existing techniques for a wide
range of decorative applications. The CAPD process
offers additional flexibility in the following areas:

(i) The controls of deposition parameters is
less stringent than magnetron sputtering or ion plating
30 processes.

(ii) The deposition temperature for compound
films can be adjusted to much lower temperatures thus
allowing the ability to coat substrates such as zinc
castings, brass and even plastics without melting the
35 substrate.

In summary the CAPD process offers many
advantages over the traditional sputtering process noted
above. However, certain decorative applications
requiring a thin film are best accomplished with a
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5 sputtering process. One such application is applying a thin coating of gold on jewelry.

This is due to the difficulty of eliminating microdroplets in gold, copper, and silver coatings in CAPD processes. Therefore, sputtering is the preferred method today for depositing a thin gold coating for decorative purposes.

Gold, however, is relatively soft. Under conditions of continuous use it develops a diffusely reflecting appearance and is simultaneously worn away. See U.S. patent number 4,591,418 (1986) to Snyder. A coating of titanium nitride (TiN) using the improved CAPD process as disclosed in U.S. patent application serial number 07/025, 207 to Randhawa, incorporated herein by reference, creates excellent color matching to gold. Thus, it is possible to deposit titanium nitride on an inexpensive jewelry piece with Randhawa's improved CAPD process and then deposit real gold over the titanium nitride. Jewelry with this unique two layer coating offers the user a real gold plated piece plus a piece with the extremely wear resistant titanium nitride undercoat. Thus, if the real gold layer partially wears away, then the color matched titanium nitride retains the look of real gold in the worn away portion of the piece.

A difficulty in sequential layers of gold and TiN is that gold and TiN adhere very poorly to one another. Until the present invention, it is believed that only two basic methods were known to create multiple gold and TiN coatings. The first method is taught by Snyder, supra, which uses at least four interleaved layers of gold and TiN. The second method is taught by U.S. patent number 4,415,421 (1983) to Sasanuma. Sasanuma teaches simultaneous sputtering by means of an electron beam three different layers. Sasanuma attempts to overcome the poor adhesion between gold and TiN by

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5 including an intermediary layer of TiN and gold between
the bottom layer of TiN and the top layer of gold.

The present invention overcomes these
difficulties and provides a convenient single system to
enable the direct coating of gold over TiN without
adhesion problems. The present invention includes an
10 advanced CAPD process and a modern magnetron sputtering
process in a single machine.

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SUMMARY OF THE INVENTION

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It is, therefore, the object of the present invention to provide a machine capable of sequentially producing a coating using the CAPD process and the magnetron sputtering process.

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Another object of the present invention is to provide the machine with a computer controlled sequencing system.

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Another object of the present invention is to provide the machine with a common substrate turntable for both processes.

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Another object of the present invention is to provide the machine with the capability to coat both sides of a workpiece simultaneously with one process and then the other process.

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Another object of the present invention is to provide the machine with a computer controlled reactant gas subsystem which can mix various gases with either process.

Another object of the present invention is to provide the machine with a variable substrate bias voltage for enhanced process control.

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Another object of the present invention is to provide the machine with a common vacuum pumping system for both processes.

Another object of the present invention is to provide the machine with a common cooling system for both processes.

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Another object of the present invention is to provide a system which allows pure gold to firmly adhere to a coating of a nitride or a carbonitride.

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Another object of the present invention is to provide a system which allows pure gold to firmly adhere to a nitride or a carbonitride or a suitably hardened substrate.

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5 Another object of the present invention is to provide a system which can simultaneously coat a substrate using a CAPD process and a magnetron sputtering process.

10 Other objects of this invention will appear from the following description and appended claims, reference being made to the accompanying drawings forming a part of this specification wherein like reference characters designate corresponding parts in the several views.

Certain terms used herein are defined below:

15 Crossover setpoint: A defined pressure in the vacuum chamber where rough pumping ceases and diffusion pump and cold trap pumping take over to reduce pressure to high vacuum.

Hi-vac: A short-hand expression for high vacuum.

MilliTorr: One thousandth of a Torr. See below.

20 Substrate: Refers to the objects being coated.

Torr: A unit of pressure; that pressure necessary to support a column of mercury one millimeter high at zero degrees Celsius and standard gravity.

25 Plasma: A collection of charged particles containing equal numbers of positive ions and electrons and which is a good conductor of electricity and is affected by a magnetic field.)

The basic magnetron sputtering process is disclosed in Thin Film Processes, supra. Improvements are disclosed in U.S. patent numbers 4,162,954 (1979) and 4,180,450 (1979) to Morrison, Jr. and assigned to the assignee of the present invention, Vac-Tec Systems, Inc. All these references are hereby incorporated herein by reference.

35 The basic CAPD process has evolved over the past twenty years. U.S. patent numbers 3,625,848 (1971) and 3,836,451 (1974) to Snaper and assigned to Vac-Tec Systems, Inc. provide the origins of the basic process. U.S. patent number 4,430,184 (1984) to Mularie and

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4,724,058 (1988) to Morrison, Jr. both assigned to Vac-
5 Tec Systems, Inc. provide improvements to the basic CAPD
process. A summary of the CAPD art is provided in
"Technical Note: A Review of Cathodic Arc Plasma
Deposition Processes And Their Applications" by H.
Randhawa and P.C. Johnson (Surface and Coatings
10 Technology, 31 (1987 pp. 303-318). Further improvements
to CAPD processing are disclosed in U.S. patent
application serial number 07/025,207 to Randhawa and
assigned to Vac-Tec Systems, Inc. All the above
references are hereby incorporated by reference herein.

15 The present invention is a production CAPD and
sputter coating system designed to deposit high
performance metallurgical coatings onto a wide variety of
substrates. It employs CAPD targets and sputter targets
to deposit thin films of material onto substrates in a
20 vacuum environment.

The sputter deposition process, using cathodes,
is a relatively high voltage, low amperage process
adaptable to depositing virtually any material. The
process bombards the target material with positive ions,
25 dislodging mainly neutral target atoms by momentum
transfer. The dislodged atoms condense into thin films
on the substrates.

The CAPD process uses a relatively high amperage
and low voltage to evaporate an electrically conductive
30 target source material and condense it onto the
substrates to form a coating.

The preferred embodiment of the present
invention employs two 5 x 24 inch (12.7 x 60.96 cm) CAPD
targets and two 3.5 x 25 inch (8.89 x 93.5 cm) sputter
35 targets to generate materials to be deposited.

A substrate fixture bearing the substrates
rotates in the chamber. Alternatively the substrate may
be variably passed in front of the targets by means of
planetary motion, oscillation, or reciprocation. A
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5 potentiometer or variable controller varies the speed of rotation according to the requirements of the deposition process.

DC bias power can be applied to the substrate fixture and substrates, during the deposition process, to enhance the movement of the target atoms toward the substrates and/or to effect the characteristics of the depositing film.

A diffusion pump, polycold trap (Meissner Trap), a cryogenic pump, or a turbomolecular pump create and maintain high vacuum in the chamber during the process. A mechanical pump evacuates the chamber to low vacuum (rough vacuum) and pumps (draws the exhaust away from) the diffusion pump or turbomolecular pump during high vacuum pumping.

A programmable logic controller (PLC) manages the process sequences. The system responds to the feedback of relevant processing parameters. Manual override is always available.

The major components of the present invention are:

1. the system main frame which supports and surrounds
 - the processing chamber,
 - the diffusion pump and polycold trap,
 - water and compressed air distribution panels,
 - mass flow controllers and valves for process gasses,
 - monitoring instruments, and
 - electrical terminal board.
2. the system control console containing the control instruments,
3. two CAPD target power supplies,
4. the mechanical pump,
5. the compressor for the polycold trap,

- 5 6. a power supply cabinet containing the
 power supplies for the targets and bias,
 7. the power distribution cabinet and
 transformer,
 8. the programmable logic controller (PLC)
 9. computer,
10 10. the software for the computer, and
 11. the software for the PLC.

A Typical CAPD Process Cycle.

15 The operator loads the fixture with substrates
 and closes the front chamber door, sealing the chamber.
 The mechanical pump reduces pressure in the chamber to
 the crossover setpoint, typically set between 80 and 150
 milliTorr.

20 The chamber roughing valve closes when the
 chamber reaches the crossover setpoint; the hi-vac valve
 opens a few seconds later. The closing of the chamber
 roughing valve isolates the mechanical pump from the
 chamber; the opening of the hi-vac exposes the chamber to
 the diffusion pump and polycold trap.

25 The pump-down cycle ends when the diffusion pump
 reduces pressure in the chamber to a preset level,
 referred to as the base pressure and typically 2×10^{-5}
 Torr. The drive motor then begins to rotate the
 substrate fixture.

30 The reduction of pressure to 2×10^{-5} Torr
 removes from the chamber most of the gas and water
 molecules which would otherwise interfere with the
 process.

35 Typically, nitrogen flows into the chamber,
 raising the pressure to 1×10^{-3} Torr or higher. The
 CAPD arc is then initiated. A high bias current
 initiates the cleaning cycle to clean the substrates with
 the sputtering action of ionized particles.

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5 The high bias cycle ends and the deposition
cycle begins. Nitrogen gas back fills the chamber to
operating pressure--a pressure between 5 and 20×10^{-3}
Torr.

10 Typically, nitrogen molecules combine with
molecules of the CAPD target (i.e. titanium) during the
reactive deposition process to form a coating of titanium
nitride on the substrates; thus, the process consumes a
portion of the nitrogen introduced into the chamber.

15 Nitrogen flows continuously into the chamber
during the deposition process, requiring constant pumping
by the high vacuum pump. The system balances the flow
rate of the nitrogen with the pumping rate to keep
pressure in the chamber at its operating pressure
setpoint.

20 The system adjusts the flow rate of nitrogen
with a mass flow controller, which compensates for the
effect of pressure on the density of nitrogen and
delivers standard volumes of gas regardless of pressure.

25 A negative voltage at the substrate accelerates
the positively-charged ions of titanium en route from the
targets. The negative voltage is called the bias voltage
and is typically in the range of -50 to -500 volts of
direct current (VDC).

30 The titanium targets are consumed during the
deposition process and must be replaced periodically.

35 CAPD targets are connected to the negative
output of the arc power supplies. Current flows from the
arc targets through a plasma to an anode. Positively
ionized particles of titanium, stripped from the target
by the current, flow toward the negatively charged
substrate, combining with nitrogen on the surface of the
substrate to form the coating.

40 The PLC shuts off the nitrogen and power to the
CAPD target sources at the conclusion of the deposition

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5 process and vents the chamber with nitrogen. When the
chamber reaches atmospheric pressure, the PLC activates
an audible signal.

Sputtering.

10 Sputtering is a relatively high voltage, low
amperage, deposition process in contrast with a CAPD
deposition process which employs relatively high
amperages and low voltages.

15 Positive ions, generated in the glow discharge
of the plasma, strike the target on the cathode and
dislodge mainly neutral target atoms by momentum
transfer.

The bombardment causes the target material to
vaporize. Atoms dislodged from the targets condense into
thin films on the substrate.

20 The targets in the preferred embodiment measure
3.5 by 25 inches and are cooled by water.

Magnetron cathodes trap the plasma in a process
chamber close to the target material by crossing
electrical and magnetic fields. The eroding action of
25 the plasma on the targets yields a high sputtering rate
per watt of power.

The preferred embodiment of the present
invention uses water cooled cathodes.

30 The operator may select from the following
parameters from the PLC for a sputtering deposition
cycle:

35 Sputter process time,
Cathode #1 power setpoint,
Cathode #2 power setpoint, and
Sputter gas pressure

The operator selects the gas from the system
control panel. Argon is the preferred gas for the
sputtering deposition process because of its mass.

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5 The sputtering deposition cycle may also be
automated. If the chamber is at base pressure, then the
operator initiates the automated process by:

1. Switching to SPUTTER from CAPD at the
deposition select panel.
2. Entering the sputter parameters at the PLC.
- 10 3. Pressing process START on the system
control panel.
4. Adding bias power if desired.

15 The completion of the above noted CAPD and
sputter process in the present invention will produce
brilliant gold plated jewelry or a variety of other
coatings on any substrate.

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BRIEF DESCRIPTION OF THE DRAWINGS

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- Fig. 1 Shows a schematic of a basic Planar Magnetron Sputtering System.
- Fig. 2 Shows a schematic of a basic Cathodic Arc Plasma Deposition (CAPD) System.
- 10 Fig. 3 Shows a schematic of the major components of the Dual Coating System of the invention.
- Fig. 4 Shows a right side elevational view of the Dual Coating System mainframe having
- 15 partial cutaways.
- Fig. 5 Shows a left side elevational view of the Dual Coating System mainframe having partial cutaways.
- Fig. 6 Shows the interior view of the right
- 20 chamber door of the Dual Coating System mainframe.
- Fig. 7 Shows the interior view of the left chamber door of the Dual Coating System mainframe.
- Fig. 8 Shows a front elevational view of the Dual
- 25 Coating System mainframe with the front chamber door and front enclosure panels cutaway.
- Fig. 9 Shows a top perspective view of the back of
- 30 the Dual Coating System mainframe having cutaways of all enclosure panels and the upper support frame.
- Fig. 10 Shows a top view of the mainframe of the Dual Coating System having all pumps removed.
- 35 Fig. 11 Shows a front elevational view of the left vacuum chamber door of the Dual Coating System mainframe having the enclosure panels removed.

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- 5 Fig. 12 Shows a front elevational view of the
 master control panel.
- Fig. 13 Shows a front perspective view of the
 vacuum chamber portion of the Dual Coating
 System mainframe. The front and right side
10 doors are removed.
- Fig. 14 Shows a front perspective view of the
 vacuum chamber and substrate fixturing.
- Fig. 15 Shows a top view cross section of the
 vacuum chamber showing all major process
 cathodes.
- 15 Fig. 16 Shows a longitudinal sectional view of the
 internally mounted sputtering cathode taken
 along line A-A of Fig. 15 which is
 coincident with the line B-B of Fig. 13.
- Fig. 17 Shows a longitudinal sectional view of the
20 internally mounted CAPD cathode taken along
 line C-C of Fig. 15 which is coincident
 with line D-D of Fig. 13.
- Fig. 18 Shows a front perspective view of a
 substrate clamp assembly for rings.
- 25 Fig. 19 Shows a software flow chart of the Program
 Logic Controller (PLC) logic.
- Fig. 20 Shows a continuation of Fig. 19.
- Fig. 21 Shows a software flow chart of the Personal
 computer (PC) logic.
- 30 Fig. 22 Shows a table of relative lusters and
 colors for various films produced by the
 present invention.

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DETAILED DESCRIPTION OF THE INVENTION

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Referring first to Fig. 1, a basic magnetron sputtering system comprises a vacuum chamber 1, a pump system 2, and a sputtering gas source 3. The vacuum chamber 1 houses a target/cathode 4 and an anode 5. Sputtering power supply 6 biases the target/cathode 4 negative and the anode 5 positive. The sputtering process uses a high voltage and low current power supply. A substrate 8 is a workpiece to be coated with a thin film 9. Substrate 8 is biased negative by substrate power supply 7.

During the sputtering process the sputtering gas source 3 supplies non-reactant gas, argon. The pump system 2 maintains a vacuum in the range of a few milliTorr to a few tens of milliTorr. The sputtering power supply 6 powers up causing a glow discharge 10 between the anode 5 and the target/cathode 4.

The glow discharge 10 causes positive ions of nonreactive gas, +, to bombard the target/cathode 4. See arrow 16. Momentum transfer causes neutral target atoms N, electrons e, and positive ions +, to dislodge from the target/cathode 4. Neutral target atoms N condense into thin film 9 on substrate 8. See arrow 14. Additionally a small percentage of positive ions + also condenses on the substrate. Positive ions + and electrons e also bombard the substrate 8 while thin film 9 is growing. See the arrows 12 and 13.

A magnet 20 is located behind the target/cathode 4. The magnet 20 creates a magnetic field around the target/cathode 4 as shown by lines 22. The magnetic field 22 is typically in the order of a few hundred gauss. Magnetic field 22 traps a substantial number of electrons e against the target/cathode surface 23. This effect of trapping the electrons e serves two basic purposes. First fewer electrons reach the substrate 8,

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5 thereby maintaining the substrate 8 at a cooler
temperature. Second the constant motion of the electrons
e at target/cathode surface 23 enhances the sputtering
yield, the emission rate of neutral particles N, from the
target/cathode surface 23. This enhanced sputtering
10 yield allows a faster growing of thin film 9 on the
substrate 8. Thus a manufacturing efficiency is realized
by reducing the time necessary to coat thin film 9 on
substrate 8.

Referring next to Fig. 2 a basic cathodic arc
plasma deposition (CAPD) system comprises a vacuum
15 chamber 1, a pump 2, and an optional gas source 30. The
vacuum chamber 1 houses a target/cathode 40 and an anode
50. CAPD power supply 60 biases the target/cathode 40
negative and the anode 50 positive. The CAPD process
uses a low voltage and high current power supply. A
20 substrate 8 is a workpiece to be coated with a thin film
90. Substrate 8 is biased negative with respect to
ground by substrate power supply 70.

During the CAPD process at least one gas 33 is
introduced into the vacuum chamber 1 by gas source 30.
25 The pump system 2 maintains a vacuum in the range of 1×10^{-4} Torr to 1×10^{-3} Torr. The substrate power supply
70 biases the substrate 8 to a high voltage in the range
of 200 to 1000 volts DC. RF voltages may be used for
non-conducting materials.

30 Next the CAPD power supply 60 applies voltage to
the target/cathode 40 and the anode 50. Next the arc
starter 44 ignites an arc 100 between the target/cathode
40 and the anode 50. An arc spot 29 forms on the
target/cathode surface 230. The arc spot 29 moves at a
35 speed of the order of a hundred meters per second on the
target/cathode surface 230. Multiple arc spots 29 are
created by using higher arc currents. The arc spot 29
moves under the control of the magnet 200 in a
predetermined pattern. The magnet 200 produces a
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5 magnetic field 220 in the range of 10-50 gauss. The arc spot(s) 29 is confined to the target/cathode surface 230 by means of an insulating border 333.

The arc spot(s) vaporizes the target/cathode 40 thus forming a stream of positive ions +, electrons e, droplets D, and neutral atoms n. The droplets D are removed from the stream by means of deposition shields 555. Droplet removal shields 555 are suitably placed in front and to the sides of target/cathode 40.

The electrons e flow to the anode 50 of the arc circuit. The positive ions + bombard the substrate 8 thereby cleaning and heating the substrate 8.

After adequate cleaning additional gas or gasses 33 are added into the vacuum chamber 1 to establish pressures in the range of 1×10^{-3} Torr to 5×10^{-2} Torr.

Next the substrate 8 is biased by substrate power supply 70 to a lower voltage in the range of 50 - 200 volts DC or RF.

Maintaining the arc 100 causes the thin film 90 to grow on the substrate 8 by the deposition of positive ions + and a small percentage of neutral atoms n. The thin film 90 thickness and the rate of deposition are controlled by varying the arc current, vacuum chamber 1 pressure, the substrate 8 bias voltage, the substrate temperature and the process time.

Referring next to Fig. 3 the Dual Coating System 400 comprises a mainframe 401, a master control panel 402, a programmable logic controller (PLC) 403, PLC software 404, a personal computer (PC) 405, PC software 406, a power distribution panel 407, arc source power supplies 408, 852, a substrate bias power supply 409, sputtering power supplies 410, 575, a control unit for the cryogenic trap 411, and a mechanical pump 452.

Referring next to Fig. 4 the right side of the Dual Coating mainframe 401 has a support skeleton 412, leveling feed 413, enclosure panels 414, 415, 416, 417,

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5 418, 419, and 420, vacuum chamber 421, front chamber door
422, right side chamber door 423, CAPD cathode 424, CAPD
anode 425, arc starter 426, process gas mass flow control
valves 427, a flow sensor 850, process gas supply pipe
428, a compressed air supply pipe 429, a compressed air
10 pressure regulator 430, a compressed air filter 431, a
cooling water supply manifold 432, a cooling water flow
control valve 434, a cooling water safety switch 435, and
an electrical terminal board 436.

Multiple chamber doors 422, 423 serve to offer
ease of access to internal components for maintenance as
15 well as flexibility in loading and unloading workpieces.
Compressed air components 429, 430, and 431 operate the
pneumatic valves in the Dual Coating System 400. Cooling
water components 432 and 434 distribute and control
cooling water to the internal chamber pipes 437. Inlet
20 port 438 and outlet port 439 in combination with internal
chamber pipes 437 and cooling water supply manifold 432
form an internal water cooled surface 400 around vacuum
chamber 421. Cooling water safety switch 435 working in
conjunction with master control panel 402 shuts off all
25 power if cooling water flow drops below a predetermined
setpoint. The electrical terminal board 436 serves as
the common termination point for all wiring to the
mainframe 401.

Referring next to Fig. 5 mainframe 401 has
30 enclosure panels 441, 442, 443, 444, 445, 419 and 420,
left side chamber door 446, cooling water filter 447,
cooling water regulator 448, sputtering cathode 449,
sputtering anode 464, and high vacuum pumping port 450.

Mainframe 401 has three chamber doors 446, 422
35 and 423 for process and maintenance flexibility. High
vacuum pumping port 450 connects to the cryogenic trap
489 and the diffusion pump 451 (Fig. 9).

Referring next to Fig. 6 the right chamber door
423 contains the same internal chamber pipes 437 as the
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5 rest of the chamber. Flexible hoses 453 and 454 carry cooling water into the right chamber door 423.

A deposition shield 455 overlays the water cooled surface 440. Deposition shield 455 is generally made of stainless steel and serves to protect the underlying surfaces from the deposition processes.

10 A viewport 456 allows users to peer into the vacuum chamber 421. A viewport shutter 457 is manually placed in front of the viewport 456 to protect the viewport 457 from the deposition process.

Referring next to Fig. 7 the left chamber door 15 446 has internal chamber pipes 437 and flexible hoses 458 and 459, and deposition shield 455. A door mounted sputtering cathode 460 is powered during the sputtering process. A door mounted CAPD cathode 461 is powered during the CAPD process. Sputtering anode 463 and CAPD 20 anode 462 are shown. Arc starter 465 starts the vacuum arc during the CAPD process.

The substrate temperature monitor 466 is an infrared sensor.

Referring next to Figure 8 vacuum chamber 421 25 houses internally mounted CAPD cathode 424 and the corresponding CAPD anode 425, the CAPD cathode mounting bracket 468 internally mounted sputtering cathode 449, and the corresponding sputtering anode 464, the sputtering cathode mounting bracket 467, door mounted 30 sputtering cathode 460 and the corresponding sputtering anode 463, a second substrate temperature infrared sensor 469, the substrate turntable 470, and the substrate mounting fixture 471.

The substrate turntable 470 rotates under the 35 control of the master control panel 402 during either the sputtering or CAPD process. The substrate mounting fixture 471 is custom designed for various substrates.

A substrate turntable drive assembly 472 comprises a drive motor 473, a drive belt 474, a 40

5 turntable drive shaft 475, a rotary vacuum seal 476,
substrate bias voltage connection 477, and the substrate
bias voltage cable 478.

Drive motor 473 is a variable speed unit
enabling precise control of the substrate turntable 470
speed. The rotary vacuum seal 476 maintains the
10 integrity of the vacuum chamber 421 during processes.
The bias voltage cable 478 connects to the substrate bias
power supply 409 (Fig. 3).

Referring next to Figure 9 the Dual Coating
System pumping assembly 479 is shown. The pumping
15 assembly 479 starts with the mechanical pump 452.
Mechanical pump 452 pumps the vacuum chamber to a
crossover pressure ranging from 60 to 90 mTorr.
Mechanical pump 452 connects to the vacuum chamber 421
through the inlet pipe 480, the inlet filter 481, the
20 connector pipe 482, the roughing valve 483 and the
chamber roughing port 484.

Thermocouple gauge 485 measures vacuum chamber
421 pressure and transmits this pressure to the master
control panel 402 (Fig. 3). When the vacuum chamber 421
25 pressure reaches a predetermined crossover pressure
ranging from 60 to 90 mTorr, the master control panel 402
closes the rouging valve 483 and opens the foreline valve
485 and opens the high vacuum valve 487. These valve
actions connect the mechanical pump 452 in series with
30 the diffusion pump 451. These serial pumps 451 and 452
are connected to the vacuum chamber 421 through the high
vacuum piping 488 and the cryogenic trap 489 and the
throttle valve 490 and the high vacuum valve 487 and the
chamber high vacuum port 450 (Fig. 5).

35 After the above noted crossover procedures are
accomplished, the mechanical pump 452 maintains the
diffusion pump foreline 491 at low pressure while the
diffusion pump 451 further reduces the vacuum chamber 421
pressure to a system base pressure ranging from 2×10^{-5}
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5 to 5×10^{-7} Torr. Simultaneously the cryogenic trap 489
condenses water vapor and other condensable gasses
thereby increasing the efficiency of the diffusion pump
451.

10 Process pressures are controlled by the master
control panel 402 operating the throttle valve 490 in
response to signals from the capacitance manometer sensor
492. The foregoing control loop is known as a downstream
pressure control system. The infrared temperature sensor
493 views the substrates 540 through viewport 469, (see
15 Fig. 8) thereby providing the temperature control signal
to the master control panel 402.

When processing is complete the vacuum chamber
421 is raised back to atmospheric pressure by means of
vent valve 494.

20 Referring next to Fig. 10 the top of the vacuum
chamber 495 is seen supported by the support skeleton
412. Water inlet 497 provides cooling water to the
internal chamber pipes 437 as supplied by the cooling
water supply manifold 432, see Fig. 4. Water outlet 499
is then returned to the cooling water supply manifold
25 432.

CAPD cathode utility plate 500 contains the
electrical power leads 501 to the anode and 502 to the
cathode of the CAPD cathode 424 and CAPD anode 425 as
seen in Fig. 4. Anode cooling water inlet 503 feeds CAPD
30 anode 425, and the anode cooling water outlet 504 returns
to the cooling water supply manifold 432. Insulating
enclosure 505 protects the CAPD cathode utility plate 500
from anode electricity. Cooling water inlet 591 supplies
cooling water from the cooling water supply manifold 432
35 (Fig. 4) to the CAPD cathode 424. An outlet 592 returns
the cooling water to the cooling water supply manifold
432.

Sputtering cathode utility plate 506 contains
the electrical power leads 507 to the anode and 508 to
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5 the cathode of the sputtering anode 464 and sputtering
cathode 449 as shown in Fig. 5. Insulating enclosure 590
insulates the sputtering cathode utility plate 506 from
electricity. Cooling water inlet 496 provides cooling
water to the sputtering cathode 449 from the cooling
10 water supply manifold 432. Cooling water return provides
the return to cooling water supply manifold 432.

Electric power for the arc starter 426 is
supplied by leads 509 and 510. Electric power for the
CAPD cathode electromagnet 530 is supplied by cable 531.

15 Shield armature 512 (see Fig. 15) is activated
by activating assembly 511. Activating assembly 511
consists of a pneumatic cylinder 515 and crank arm 516.

Vacuum chamber 421 pressure is sensed and
transmitted by pirani gauge 517, thermocouple gauge 518
and ion gauge 519. Pirani type gauge 517 measures
20 pressures ranging from atmospheric to 1 mTorr.
Thermocouple gauge 485 measures pressures ranging from
atmospheric to 1 mTorr. Ion gauge 519 measures pressures
ranging from 1 mTorr - 0.0001 mTorr. Thermocouple gauge
518 triggers the master control panel 401 for switching
25 the ion gauge 519 on.

Referring next to Fig. 11 the vacuum chamber 421
is seen supported by the support skeleton 412. The left
vacuum chamber door 520 opens for loading and
maintenance. An enclosure panel 521 is cut away. Water
30 inlet 522 and water outlet 523 feed the internal chamber
pipes 437 from the cooling water supply manifold 432.
Water inlet 593 supplies cooling water from the cooling
water supply manifold 432 to the door mounted CAPD
cathode 461. Outlet 594 returns the cooling water
35 through the cooling water supply manifold 432.

The door mounted CAPD cathode 461 is mounted
inside CAPD door enclosure 524. Power to the door
mounted CAPD cathode is supplied by lead 525. Power to
the CAPD anode 462 is supplied by lead 526. Cooling
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5 water inlet 527 supplies cooling water from the cooling
water supply manifold 432 to the door mounted CAPD anode
462 as shown in Fig. 7. Cooling water return 528
supplies the return to cooling water supply manifold 432.

Electrical insulating enclosure 529 electrically
isolates the door mounted CAPD anode 462. Electrical
10 insulating enclosure 532 electrically isolates the door
mounted CAPD cathode 461. CAPD electromagnet 530 (Fig.
17) is powered by cable 533. Water inlet 534 supplies
cooling water from the cooling water supply manifold 432
to the door mounted sputtering cathode 460 (see Fig. 7).
15 The water returns via water outlet 535. Lead 536 powers
the door mounted sputtering cathode 461. Leads 537 and
538 power the arc starter 465 (Fig. 7).

An infrared sensor 539 measures the substrate
540 temperature as shown in Fig. 8. The infrared sensor
539 consists of a lens assembly 541, a fiber optic cable
542, and the infrared sensing unit 543. Infrared sensing
unit 543 measures and transmits the substrate 540
temperature to the master control panel 402. High
intensity light source 544 calibrates lens assembly 541.
25 Enclosure safety switches 560 prevent operation if an
enclosure panel is ajar.

Referring next to Fig. 12 the master control
panel 402 consists of a substrate temperature transmitter
545 which indicates temperatures from the infrared
30 sensors 493 and 543 by means of gauge 546.

Substrate temperature transmitter 545 switches
between infrared sensing units 493 and 543 and
subsequently transmits the substrate temperatures to the
programmable logic controller (PLC) 403.

35 The vacuum chamber pressure monitoring panel 547
consists of a thermocouple gauge indicator 548 which
senses inputs from the thermocouple sensor 518 (Fig. 10).
The ion gauge indicator 549 senses inputs from the ion
tube 519 (Fig. 10). The pirani gauge indicator 550
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senses inputs from the pirani gauge sensor 517.
5 Additionally the pirani gauge indicator 550 transmits signals to the valve control panel 551 which in turn controls the roughing valve 483, the high vacuum valve 487, and the vent valve 494. The valve control panel 551 also controls the diffusion pump foreline valve 486 and
10 the throttle valve 490 (Fig. 9).

The system control panel 552 consists of a drive motor 473 speed indicator/controller 553. Additionally the system control panel 552 provides a manual/automatic mode of operation by means of selector switch 554.
15 Manual control switch 558 offers manual control of the process gas mass flow control valve 427 (Fig. 4). To initiate either the CAPD or sputtering process master start switch 556 must be switched "on". Process termination may be manually accomplished by switching the
20 process stop switch 557 "off". A process status board 559 indicates the statuses of vacuum chamber 421 pressure range, cooling water safety switch 435 (Fig. 4), enclosure safety switch 560 (Fig. 11) status, drive motor 473 overtorque indicator (Fig. 8), and the overall
25 process enable status indicator.

The process selection panel 561 provides selection of either the CAPD or sputtering process by means of selector switch 562.

The arc control panel 563 displays the
30 respective CAPD voltages and amperages by means of indicators 564, 565, 566, and 567. The operator may manually select whether to use one or both of the CAPD cathodes 424/461 by means of selector switches 568 and 569. The CAPD arc power may be manually controlled by
35 potentiometers 570 and 571.

Varying substrate 540 surface areas require varying bias power requirements. Substrate bias power control module 572 controls the bias power supply 409 and indicates bias voltage by means of indicator 851. The
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5 internal sputtering cathode controls the internal
sputtering power supply 410. The door mounted sputtering
cathode power control module 574 controls the door
mounted sputtering power supply 575 (Fig. 3). Power
indicators 853 and 854 integral to the sputtering cathode
control modules 573 and 574 indicate the electrical power
10 levels of the respective sputtering cathodes.

The capacitance manometer sensor 492 (Fig. 9)
transmits a signal to the capacitance manometer
controller 576. The vacuum chamber 421 pressure is
indicated by the indicator 577 integral to the
15 capacitance manometer controller 576. Additionally the
capacitance manometer controller 576 provides an input
signal to the process gas controller 578.

The process gas controller 578 displays the
process gas flow by means of indicator 579. Flow sensor
20 850 (Fig. 4) supplies input to the indicator 579. The
process gas controller 578 modulates process gas mass
flow control valve 427 in response to signals from the
capacitance manometer controller 576, thereby controlling
vacuum chamber 421 pressure. The foregoing control loop
25 constitutes an upstream pressure control system.

Support panel 581 houses the PLC input module
582. PLC input module 582 is used to key enter variable
data into the PLC 403. The PLC 403 contains PLC software
404 which automatically can control all the CAPD and
30 sputtering process functions for the Dual Coating System
400.

Figures 13, 14 and 15 show the spatial
relationships of the main operating components of the
Dual Coating System 400. Fig. 13 shows the substrate
35 turntable 470. The internally mounted CAPD cathode 424
is supported above and in close proximity to the
substrate turntable 470 by means of the CAPD cathode
mounting bracket 468. The corresponding CAPD anode 425
and arc starter 426 are commonly mounted to the same CAPD
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5 cathode mounting bracket 468. Utility cable 596 and 597
house cooling water pipes and electrical conductors
serving the internally mounted CAPD cathode 424.

The internally mounted sputtering cathode 449
and corresponding anode 464 are mounted on the sputtering
cathode mounting bracket 467. Corresponding utility
10 cables 598 and 599 house cooling water pipes and
electrical conductors serving the internally mounted
sputtering cathode 449.

The door mounted sputtering cathode 460 and its
corresponding anode 463 faces the internally mounted
15 sputtering cathode 449 such that simultaneous sputtering
coating on both sides of the substrate 540 can be
accomplished.

The door mounted CAPD cathode 461 coats the
outside of the substrate 540 while the internally mounted
20 CAPD cathode coats the inside of the substrate 540. The
corresponding CAPD arc starter 465 and anode 462 are
mounted on the same left chamber door 446. The substrate
temperature monitor 466 protrudes beyond the deposition
shield 455.

25 Fig. 14 shows a typical mounting arrangement for
small substrates such as rings. The substrate turntable
470 is in electrical contact with the substrate mounting
fixture 471 which in turn is in electrical contact with
the substrate 540.

30 Fig. 15 shows in dotted lines how the shield
armature 512 moves the sputtering cathode shields 513 and
514 away from the sputtering cathodes 449 and 460 during
the sputter coating. The shield armature 512 shown in
solid lines moves the sputtering cathode shields 513 and
35 514 in front of the sputtering cathodes 449 and 460 to
protect them from being coated during the CAPD process.

An alternate embodiment (not shown) uses RF
sputtering cathodes either in addition to or in lieu of

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the magnetron sputtering cathodes 449 and 460.

5 Additionally RF substrate biasing (not shown) may be used.

A second alternate embodiment (not shown) uses diode sputtering either in addition to or in lieu of the magnetron sputtering cathodes 449 and 460.

10 The droplet removal shields 555 (see Fig. 2) serve to remove all droplets D from the stream of positive ions, electrons, and neutral atoms vaporizing from the door mounted CAPD cathode 461 and the internally mounted CAPD cathode 424.

15 Referring to Figure 2 the droplets D comprise molten metal particles which if allowed to land on the substrate 8 results in rough and low luster films. This is unacceptable for decorative applications. It has been experimentally determined that droplets D are emitted at
20 angles θ or less. θ has been found to be 30 degrees or less when the CAPD target 615 (Fig. 17) has a minimal area of ten square inches. The distance 557 of the droplet removal shields 555 and the opening 556 are selected to prohibit the droplets D from reaching the
25 substrate 8 (Fig. 2).

The main purpose of the present invention is to provide a film having a high luster and a consistent color controllable to match various gold colors. Fig. 22 shows a sampling of films produced by the present
30 invention. Sequence Numbers 8 and 9 list the 10 carat and 24 carat gold characteristics used herein as a standard. L^* denotes the luster or brilliance of the film as measured per the CIE Lab color coordinates. a^* denotes a range of red to green contents in the film.
35 Positive a^* values denote red contents and negative a^* values denotes green contents in the film. b^* denotes a range of yellow to blue contents in the film. The

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5 positive b* values indicate a high yellow content in the film. Negative values would indicate a blue content in the film.

Sequence numbers 1 through 7 show specific film characteristics produced by the CAPD process used in the Dual Coating System 400. Referring to Fig. 19 Block 1006
10 varies the ratios of two process gasses (Fig. 2, 33) which comprise acetylene as a source of carbon, and nitrogen. Suitably adjusting the ratios of carbon and nitrogen in the titanium and zirconium based films results in the excellent matching of luster and color
15 film characteristics relative to gold as shown in Fig. 22. Thus in the typical Dual Coating System 400 operation a CAPD film is produced from the above noted Fig. 22 Sequence Numbers 1 through 7. Next a gold film may be applied using the sputtering process as shown in
20 Fig. 1.

The preferred embodiment produces in sequence the above noted two films during a single vacuum cycle (Fig. 19 Block 1004). The adhesion of a second film consisting of gold on top of a CAPD deposited film taken
25 from the selection in Fig. 22 Sequence Numbers 1 through 7 is commercially acceptable. A commercially acceptable adhesion is determined by using a Scotch Tape Pull test. This test results in no gold removal.

The ultimate purpose of the Dual Coating System
30 400 is to provide a single system which enables the direct coating of gold over TiN or ZrN without adhesion problems. In practice the gold wears off the substrate 8 (Fig. 1) thus exposing the TiN or ZrN film underneath. It is critical in the practice of the present invention
35 that the substrate 8 maintain the same appearance as the gold film wears off. Thus the relative values in Fig. 22 Sequence Numbers 1 through 7 in relation to Sequence Numbers 8 and 9 are critical to the successful practice of the present invention.
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Fig. 16 shows the internally mounted sputtering cathode 449 and corresponding anode 464 as seen in Figures 5, 8, 13 and 15. Internally mounted sputtering cathode 449 is comprised of cathode body 600, sputtering target 601, and magnet 602. Clamp 603 fastens the target 601 to the cathode body 600 and completes their electrical continuity. Lead 508 powers the internally mounted sputtering cathode 449. Cooling water inlet 496 supplies water to the cooling water passage 604 thereby cooling the target 601. Outlet 498 returns the cooling water to the cooling water supply manifold 432 (Fig. 4). O-ring 605 provides a waterproof seal between the target 601 and cathode body 600.

Corresponding sputtering anode 464 comprises an anode body 605, a dark space shield 606 and a utility hub 607. The dark space shield 606 restricts the plasma discharge to the target 601. The dark space shield is affixed to the anode body 605 by means of screws 608. The sputtering anode 464 is insulated from the internally mounted sputtering cathode 449 by means of insulators 610, Teflon bolts 609, and insulating ring 611. O-rings 612 and 613 maintain a vacuum seal between utility conduits 598 and 599 and the vacuum chamber 421.

Fig. 17 shows the internally mounted CAPD cathode 424 as seen in Figures 4, 8, 13, and 15. Internally mounted CAPD cathode 424 is comprised of cathode body 614, CAPD target 615, target edge insulating strip 616, cathode body insulation 617, cathode shroud 618, and magnet 530. Cathode shroud 618 is insulated from the cathode body 614 by means of insulators 619, 620 and 621 and Teflon screws 622. Target edge insulating strip 616 is fastened to the CAPD target 615 by means of insulating fasteners 623. O-ring 624 provides a vacuum and water seal between the cathode body 614 and the CAPD target 615. Cooling water passage 625 is supplied with cooling water from inlet 591, thereby cooling the CAPD

5 target 615. Outlet 592 returns the cooling water to the
cooling water supply manifold 432. O-rings 626, 627,
628, 629, 630 and 631 maintain a vacuum seal between the
cathode body 614 and cathode shroud 618 and the utility
cables 596, 597 and 632. Utility cables 596, 597 and 632
10 connect to the cathode shroud 618 by means of connection
hubs 633, 634 and 635.

Power to the electromagnet 530 is supplied by
cable 531. Gasket 636 maintains a water tight seal
between the electromagnet 530 and the cathode body 614.
Power to the CAPD cathode 424 is supplied by lead 637 and
15 638 via connectors 639 and 640. Insulating sleeves 641
and 642 insulate connectors 639 and 640 from the cathode
shroud 618.

Referring next to Fig. 18 the substrate
turntable 470 has a mounting surface 702 which supports
20 the substrate mounting fixture 471. The substrate
mounting fixture 471 further comprises a base column 701,
and a variable length rod 704. A substrate clamp 703 is
affixed to the variable length rod 704. Substrate clamp
703 has a flexible spring consistency. A triangular
25 shape supports the substrate 540 in three spots. A ring,
bracelet, earring or similar shaped substrate can be
firmly secured with minimal contact against the substrate
clamp 703.

Referring next to Fig. 3, the PLC 403 has the
30 following basic hardware capabilities:

- Memory for storage of an operating system
- Memory for storage of a process program
- Logic module for process program execution
- Logic module for input/output control

35 The PLC software 404 has the following basic functional
capabilities:

- An operating system for controlling the PLC
hardware
- A process program ladder logic module

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5 Referring next to Fig. 19 block 1000 shows the
PLC operating system starting up and checking hardware
diagnostics to ensure a fully functional PLC exists
before proceeding further.

Block 1001 shows the PLC reading all of the Dual
Coating System 400 signal inputs including substrate
10 temperature transmitter 545, cooling water safety switch
435 status, enclosure panels 414, 415, 416, 417, 418, 419
and 420 status, thermocouple sensor 518 measuring vacuum
pressure, ion tube 519, pirani gauge sensor 517, valve
control panel 551, drive motor 473 speed
15 indicator/controller 553, manual/automatic selector
switch 554, CAPD or sputtering process master start
switch 556, selector switch 562, process termination
switch 557, cooling water safety switch 435, enclosure
safety switch 560, voltage and amperage indicators 564,
20 565, 566, and 567, CAPD cathode selector switches 568 and
569, substrate bias control module 572, internal
sputtering power supply 410, door mounted sputtering
cathode power control module 574, power indicators 853
and 854, capacitance manometer sensor 492, and the
25 process gas controller 578.

Block 1002 shows the PLC 403 receiving variable
recipe data from either the PC 405 or PLC input module
582.

30 Additionally the PLC 403 can send data to the PC
405 or to the PLC input module 582.

Block 1003 checks for a safe system including
cooling water safety switch 435 status, enclosure panels
414, 415, 416, 417, 418, 419 and 420 all closed, and the
thermocouple gauge indicator 548 which must show a vacuum
35 exists before proceeding further. Therefore, the program
logic first assures that the Dual Coating System 400 has
adequate water flow and has all safety covers in place
and has all doors and openings sealed thereby ensuring a
secured vacuum chamber 421.

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5 Block 1004 shows the logic for the sequencing of
the mechanical pump 452, diffusion pump 451 and the
cryogenic trap 489.

 Block 1005 shows the logic for selecting whether
to proceed with CAPD or sputtering by reading selector
switch 562.

10 Block 1006 shows the logic for controlling the
CAPD process gas by means of the process gas controller
578 which controls the mass flow control valves 427, and
variable input process parameters from Block 1002. The
15 PLC logic generates an error signal for pressure
deviating from set point, and adjusts the mass flow
control valves 427 accordingly.

 Block 1007 shows the first process specific step
for the CAPD process. This first step requires enabling
the CAPD power supplies 408 and/or 852. Next the CAPD
20 magnet 530 is enabled. Next the substrate bias power
supply 409 is enabled. Next the substrate turntable 470
is activated. Next the substrate bias power supply 409
is controlled to the command voltage as received from
Block 1002. Next the arc starter(s) 426, 465 ignite the
25 arc(s).

 The user has inputted a substrate temperature
parameter into Block 1002. Now in Block 1008 the
substrate temperature is brought up to setpoint by means
of varying the CAPD power supplies 408 and 852, and the
30 substrate bias power supply 409.

 Blocks 1009, 1010, 1011, 1012 execute time
versus power consumption and substrate temperature
setpoint recipes which have been input into Block 1002.

35 Block 1012 terminates the CAPD process after a
predetermined amp hour setpoint as received from Block
1002.

 Block 1013 dictates whether to proceed with a
sputtering process as predetermined from Block 1002.

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5 Block 1014 proceeds to an orderly shutdown by
allowing the internal chamber pipes 437 to cool the
substrate 540 to a predetermined temperature as dictated
by Block 1002.

 Block 1015 executes either an atmospheric vent
by opening vent valve 494, or by introducing process gas
10 by means of process gas control valves 427.

 The sputtering process is started in Block 1016
by introducing process gases by means of the process gas
controller 578.

 Next Blocks 1017, 1018 move the sputtering
15 cathode shields 513, 514 in front of the sputtering
cathodes 464 and 463. Block 1017 proceeds to power the
sputtering power supplies 410, 575 in order to sputter
clean the sputtering target/cathodes 449 and 460. Time
duration for sputter cleaning is dictated by Block 1002.

20 Next Block 1019 removes the sputtering cathode
shields 513 and 514 away from the sputtering target
cathodes 449 and 460. The substrate turntable 470 is
activated.

 Next Block 1020 sputters for a predetermined
25 time and sputtering power supplies 410, 575 supply power
output as determined by block 1002.

 Sputtering terminates with Blocks 1014 and 1015.

 Block 1100 shows the PC running executive
software and receiving variable process recipes.
30 Variable process recipes include all time, temperature,
power, flow and pressure variables the user desires for
his process. Block 1101 shows the CRT on the PC
displaying the variable input recipes. An optional print
output Block 1102 is shown. Alternatively the variable
35 process recipes may be entered by means of the PLC input
module 582.

 Block 1103, shows the PC translating the
variable input recipes from engineering units to PLC

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5 format data. Block 1104 shows the PC 405 storing and
retrieving the variable input recipes.

 Block 1105 controls all PC/PLC communications.
Block 1106 shows the PLC 403 receiving the variable input
recipes. Additionally the PLC 403 can be commanded by
the PC 405 to transmit measured process parameters for
10 display and storage by the PC 405.

 Variable process recipes can be input into Block
1100 concurrently with the execution of measured process
parameter displays and storage in Blocks 1101, 1102 and
1104.

15 The best mode for practicing the above noted
computer art utilizes a Texas Instruments Series 500 PLC
Model 530 C-1102.. The PC used herein is an IBM (or
compatible) using a Microsoft operating system, MS-DOS,
and EGA/VGA graphics. EGA/VGA graphics allow sixteen
20 color displays, primitives and text. Asynchronous serial
communications between the PLC and the PC utilize Texas
Instruments Task Codes and assembly language routines.

 The PLC ladder logic software is written using
the Texas Instruments Tisoft Ladder Editor. The PC
25 executive software is written in the "C" language using
the Microsoft C compiler.

 The executive software for the PC is menu driven
thereby allowing the screen to prompt the user into
entering variable recipes in engineering units. On line
30 "help" prompts are available to the user as an exit from
all screens. The executive software accepts all data in
engineering units and converts all data to PLC machine
readable data using "C" language subroutines.

 The CRT Block 1101, printer Block 1102 and disk
35 Block 1104 can receive and display or print or store all
variable input process parameters in real time.

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CLAIMS

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I Claim:

1. An apparatus for coating a substrate,
comprising:
 - (a) a vacuum chamber;
 - 10 (b) a pumping system for creating a vacuum
inside the vacuum chamber;
 - (c) a substrate;
 - (d) a sputtering target/cathode with an
erosion face;
 - 15 (e) magnetic means located adjacent to the
sputtering target/cathode on the
opposite side of said erosion face of
the sputtering target/cathode;
 - 20 (f) a sputtering anode for generating a
plasma discharge for the sputtering
target/cathode;
 - (g) a sputtering power supply for
generating an electric circuit between
said sputtering target/cathode and
25 said anode for the sputtering
target/cathode;
 - (h) means for introducing and controlling
a process gas in the vacuum chamber to
cause a glow discharge between the
30 sputtering target/cathode and the
anode, thereby vaporizing the erosion
face and depositing a sputtering
coating on the substrate;
 - (i) a CAPD target/cathode, including an
35 erosion face;
 - (j) a CAPD anode for the CAPD
target/cathode;

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(k) a CAPD power supply for generating an electric circuit between said CAPD target/cathode and said CAPD anode;

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(l) means for starting an arc between said CAPD target/cathode and CAPD anode to cause an arc spot on the erosion face, thereby vaporizing the CAPD target/cathode erosion face and depositing a CAPD coating on the substrate; and

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(m) means for sequentially controlling the application of a plurality of thin film coatings on the substrate.

2. The apparatus for coating a substrate in claim one, further comprising:

20

(a) means for mounting the substrate inside the vacuum chamber;

(b) means for electrically biasing the substrate;

25

(c) means for measuring the substrate electrical bias;

(d) means for measuring the power of the sputtering power supply;

(e) means for controlling the process gas pressure;

30

(f) means for measuring the substrate temperature;

(g) means for controlling the substrate temperature;

(h) means for measuring the power of the CAPD power supply; and

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(i) means for cooling the vacuum chamber and the sputtering target/cathode and the CAPD target/cathode.

3. The apparatus for coating a substrate in claim one, further comprising a turntable in said vacuum

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5 chamber, which turntable is in electrical continuity with the substrate; and an upright substrate support stand on said turntable.

10 4. The apparatus for coating a substrate in claim three, wherein said upright support stand further comprises a clamp having a spring which contacts the substrate.

5. The apparatus for coating a substrate in claim three, further comprising a substrate bias power supply; a rotary vacuum seal for the turntable; and interconnecting power connections.

15 6. The apparatus for coating a substrate in claim one, further comprising means for electrically biasing the substrate; and a substrate electrical bias indicator integral to the electrically biasing means.

20 7. The apparatus for coating a substrate in claim one, further comprising means for measuring the power of the sputtering power supply and a power indicator integral to the sputtering power supply.

25 8. The apparatus for coating a substrate in claim one, wherein the means for introducing and controlling a process gas includes a capacitance manometer, a mass flow controller, a mass flow gas control valve, and a throttle valve.

30 9. The apparatus for coating a substrate in claim eight, wherein the means for introducing and controlling the process gas further includes an upstream pressure control loop.

35 10. The apparatus for coating a substrate in claim eight, wherein the means for introducing and controlling the process gas further includes a downstream pressure control loop.

11. The apparatus for coating a substrate in claim one, further comprising an infrared sensor; and an indicator for measuring the substrate temperature.

5 12. The apparatus for coating a substrate in
claim five, further comprising means to vary the rate of
using CAPD sputtering; means to vary the power of the
substrate bias power supplies; and means to vary the
speed of the turntable.

10 13. The apparatus for coating a substrate in
claim eleven, further comprising means for measuring the
power of the CAPD power supply; and a power indicator to
the CAPD power supply.

15 14. The apparatus for coating a substrate in
claim two, wherein the means for starting the arc between
said CAPD target/cathode and CAPD anode further comprise
an arc starter.

20 15. The apparatus for coating a substrate in
claim one, further comprising interconnected cooling
water pipes for cooling the vacuum chamber and the
sputtering target/cathode and the CAPD target/cathode.

25 16. The apparatus for coating a substrate in
claim fifteen, wherein the interconnected cooling water
pipes include a network of cooling water pipes located
adjacent to the surface of the vacuum chamber, the
sputtering target/cathode and the CAPD target/cathode.

30 17. The apparatus for coating a substrate of
claim one, wherein the vacuum chamber further comprises
three doors, internal chamber cooling water pipes, a
deposition shield, and a viewport.

35 18. The apparatus for coating a substrate in
claim one, wherein the pumping system further comprises a
mechanical pump, a diffusion pump and a cryogenic trap.

40 19. The apparatus for coating a substrate in
claim one, further comprising a substrate with an array
of workpieces having two or more sides.

45 20. The apparatus for coating a substrate in
claim one, further comprising a second sputtering
target/cathode and a second CAPD target/cathode, so that
the substrate can be simultaneously coated on both sides

5 by either at least two sputtering target/cathodes or at
least two CAPD target cathodes.

21. The apparatus for coating a substrate in
claim one, wherein the sputtering target/cathode further
comprises movable shields, thereby protecting the
sputtering target/cathode from being coated while the
10 CAPD target/cathode is operating.

22. The apparatus for coating a substrate in
claim one, wherein the sputtering target/cathode further
comprises a cathode body, the magnetic means, cooling
water passages adjacent the sputtering target, and
15 connecting means for the aforesaid items.

23. The apparatus for coating a substrate in
claim twenty one, wherein the sputtering anode further
comprises an anode body integral to the cathode body, and
a dark space shield, thereby restricting the plasma
20 discharge to the sputtering target/cathode.

24. The apparatus for coating a substrate in
claim one, wherein the CAPD target/cathode further
comprises a cathode body, a target edge insulating strip,
a CAPD magnet behind the erosion face, cooling water
25 passages adjacent the target, and connecting means for
the aforesaid items.

25. The apparatus for coating a substrate in
claim one, wherein the CAPD anode further comprises
integral cooling water pipes.

30 26. The apparatus for coating a substrate in
claim one, wherein the sputtering target/cathode erosion
face is inside the vacuum chamber.

27. The apparatus for coating a substrate in
claim one, wherein the CAPD target/cathode erosion face
35 is inside the vacuum chamber.

28. The apparatus for coating a substrate in
claim one, wherein the CAPD target/cathode further
comprises means for removing droplets from the vaporizing
CAPD target/cathode erosion face.

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5 29. The apparatus for coating a substrate in
claim twenty eight, wherein the means for removing
droplets from the vaporizing CAPD target/cathode erosion
face further comprises a droplet removal shield having a
location in front of the CAPD target/cathode erosion
10 face, thereby preventing droplets from reaching the
substrate.

30. The apparatus for coating a substrate in
claim one, wherein the CAPD coating has substantially the
same luster and color of gold.

15 31. The apparatus for coating a substrate in
claim one, wherein the CAPD coating is a metal selected
from the group consisting of titanium, zirconium, carbon
and nitrogen.

20 32. The apparatus for coating a substrate in
claim one, wherein the sputtering coating and the CAPD
coating are sequentially produced in the vacuum chamber
without eliminating the vacuum.

25 33. The apparatus for coating a substrate of
claim two, further comprising a computer system, wherein
the computer system monitors and controls the pumping
system, the process gas system, the means for
electrically biasing the substrate, the means for
controlling the substrate temperature, the means for
cooling the vacuum chamber, and the sputtering and CAPD
power supplies.

30 34. The apparatus for coating a substrate of
claim thirty three, wherein the computer system further
comprises a program logic computer (PLC) and a personal
computer (PC) interconnected to the PLC.

35 35. The apparatus for coating a substrate of
claim thirty four, wherein the PLC contains ladder logic
software for monitoring and controlling the pumping
system, the process gas system, the means for
electrically biasing the substrate, the means for

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5 controlling the substrate temperature, the means for
cooling the vacuum chamber, and the sputtering and CAPD
power supplies.

36. The apparatus for coating a substrate of
claim thirty five, wherein the PC further comprises
executive software having menus for entering variable
10 parameters into the PLC ladder logic software, and
further comprising software to indicate the status of the
PLC ladder logic software.

37. The apparatus for coating a substrate of
claim thirty six, wherein the executive software further
15 comprises screen prompted table inputs for entering
variable parameters into the PLC ladder logic software.

38. The apparatus for coating a substrate of
claim thirty six, wherein the executive software further
comprises multicolor high resolution graphics.

20 39. A computer system, comprising:
(a) a PLC;
(b) a PC;
(c) means for communicating data between
the PLC and the PC;
25 (d) means for inputting variable process
parameters from a CAPD and sputtering
dual coating system; said variable
process parameters including pumping
system data, process gas data,
30 substrate biasing data, substrate
temperature data, vacuum chamber
cooling data, and CAPD and sputtering
power supply data;
(e) means for inputting variable process
35 recipes from a user; and
(f) means for sending control signals to
the CAPD and sputtering dual coating
system, thereby controlling the

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variable process parameters to the values of the variable process recipes.

40. A method for depositing multiple thin film coatings on a substrate, comprising the steps of:

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- (a) placing the substrate in a chamber;
- (b) evacuating the chamber;
- (c) activating a CAPD target/cathode in the chamber;

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- (d) depositing a thin CAPD film on the substrate;

- (e) injecting a process gas into the chamber;

- (f) activating a magnetron sputtering target/cathode in the chamber;

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- (g) creating a plasma discharge in the chamber; and

- (h) depositing a thin sputtering film on the substrate.

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41. The method for depositing multiple thin film coatings on a substrate in claim forty, further comprising the steps of:

- (i) cooling the chamber;

- (j) controlling all the foregoing process steps by means of a computer system.

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42. The method for depositing multiple thin film coatings on a substrate in claim forty, further comprising the steps of:

- (k) shielding the CAPD droplets from the substrate.

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43. The method for depositing multiple thin film coatings on a substrate in claim forty, further comprising the steps of:

- (l) controlling the thin CAPD film to be substantially the same luster and color as gold.

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5 44. The method for depositing multiple thin
film coatings on a substrate in claim forty, further
comprising the steps of:

- (m) controlling the thin sputtering film
to be firmly adhered to the thin CAPD
film.

10 45. The method for depositing multiple thin
film coatings on a substrate in claim forty, wherein the
chamber vacuum is not broken between the CAPD deposition
and the spotting deposition except by injecting of the
process gas.

15 46. An apparatus for coating a substrate
comprising:

- (a) a vacuum chamber;
- (b) gas process means for creating a
vacuum and for introducing and
20 controlling process gas within the
vacuum chamber;
- (c) CAPD means in the vacuum chamber;
- (d) magnetron sputtering means in the
vacuum chamber; and
- 25 (e) means for sequentially controlling the
application of a plurality of thin
films by said CAPD means and magnetron
sputtering means.

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[received by the International Bureau on 2 October 1989 (02.10.89)
original claims 1,2,12,14,19 and 45 amended;
other claims unchanged (4 pages)]

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I Claim:

1. An apparatus for coating a substrate, comprising:
 - (a) a vacuum chamber;
 - (b) a pumping system for creating a vacuum
inside the vacuum chamber;
 - 10 (c) means for mounting the substrate inside
the vacuum chamber;
 - (d) a sputtering target/cathode with an
erosion face inside of said vacuum chamber;
 - 15 (e) magnetic means located adjacent to the
sputtering target/cathode on the
opposite side of said erosion face of
the sputtering target/cathode;
 - (f) a sputtering anode for generating a
plasma discharge for the sputtering
20 target/cathode;
 - (g) a sputtering power supply for
generating an electric circuit between
said sputtering target/cathode and
said anode for the sputtering
25 target/cathode;
 - (h) means for introducing and controlling
a process gas in the vacuum chamber to
cause a glow discharge between the
sputtering target/cathode and the
30 anode, thereby vaporizing the erosion
face and depositing a sputtering
coating on the substrate;
 - (i) a CAPD target/cathode, including an
erosion face inside of said vacuum chamber;
 - 35 (j) a CAPD anode for the CAPD target/cathode;

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- 5 (k) a CAPD power supply for generating an electric circuit between said CAPD target/cathode and said CAPD anode;
- 10 (l) means for starting an arc between said CAPD target/cathode and CAPD anode to cause an arc spot on the erosion face, thereby vaporizing the CAPD target/cathode erosion face and depositing a CAPD coating on the substrate; and
- 15 (m) means for sequentially controlling the application of a plurality of thin film coatings on the substrate.

2. The apparatus for coating a substrate in claim one, further comprising:

- 20 (a) means for electrically biasing the substrate;
- (b) means for measuring the substrate electrical bias;
- (c) means for measuring the power of the sputtering power supply;
- 25 (d) means for controlling the process gas pressure;
- (e) means for measuring the substrate temperature;
- (f) means for controlling the substrate temperature;
- 30 (g) means for measuring the power of the CAPD power supply; and
- (h) means for cooling the vacuum chamber and the sputtering target/cathode and the CAPD target/cathode.
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3. The apparatus for coating a substrate in claim one, further comprising a turntable in said vacuum

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12. The apparatus for coating a substrate in
5 claim five, further comprising means to vary the rate of
CAPD and sputtering; means to vary the power of the
substrate bias power supplies; and means to vary the
speed of the turntable.

13. The apparatus for coating a substrate in
10 claim eleven, further comprising means for measuring the
power of the CAPD power supply; and a power indicator to
the CAPD power supply.

14. The apparatus for coating a substrate in
claim one, wherein the means for starting the arc between
15 said CAPD target/cathode and CAPD anode further comprise
an arc starter.

15. The apparatus for coating a substrate in
claim one, further comprising interconnected cooling
water pipes for cooling the vacuum chamber and the
20 sputtering target/cathode and the CAPD target/cathode.

16. The apparatus for coating a substrate in
claim fifteen, wherein the interconnected cooling water
pipes include a network of cooling water pipes located
adjacent to the surface of the vacuum chamber, the
25 sputtering target/cathode and the CAPD target/cathode.

17. The apparatus for coating a substrate of
claim one, wherein the vacuum chamber further comprises
three doors, internal chamber cooling water pipes, a
deposition shield, and a viewport.

18. The apparatus for coating a substrate in
30 claim one, wherein the pumping system further comprises a
mechanical pump, a diffusion pump and a cryogenic trap.

19. The apparatus for coating a substrate in
claim one, further comprising a substrate holder for
35 holding an array of workpieces having two or more sides.

20. The apparatus for coating a substrate in
claim one, further comprising a second sputtering
target/cathode and a second CAPD target/cathode, so that
the substrate can be simultaneously coated on both sides

5 44. The method for depositing multiple thin
film coatings on a substrate in claim forty, further
comprising the steps of:

- (m) controlling the thin sputtering film
to be firmly adhered to the thin CAPD
film.

10 45. The method for depositing multiple thin
film coatings on a substrate in claim forty, wherein the
chamber vacuum is not broken between the CAPD deposition
and the sputtering deposition except by injecting of the
process gas.

15 46. An apparatus for coating a substrate
comprising:

- (a) a vacuum chamber;
- (b) gas process means for creating a
vacuum and for introducing and
20 controlling process gas within the
vacuum chamber;
- (c) CAPD means in the vacuum chamber;
- (d) magnetron sputtering means in the
vacuum chamber; and
- 25 (e) means for sequentially controlling the
application of a plurality of thin
films by said CAPD means and magnetron
sputtering means.

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STATEMENT UNDER ARTICLE 19

Following receipt of the International Search Report, the accompanying Amendments of Claims is hereby submitted pursuant to Article 19 of the PCT. Pursuant to Article 19(1) this statement of explanation is respectfully submitted.

Claim 1: Claim 1 has been amended in order to more particularly point out and distinctly claim the subject matter of the invention. In particular, elements (d) and (i) are specifically related to the other elements claimed by clarifying that they are found inside of the vacuum chamber. Also, element (c) "a substrate" is replaced with the means for mounting the substrate inside the vacuum chamber.

Claim 2: The means for mounting the substrate were moved to the independent claim 1 and were therefore removed from dependent claim 2.

Claim 12: Claim 12 has been amended to correct a typographical error.

Claim 14: This claim may depend from independent claim 1 as well as from dependent claim 2.

Claim 19: Claim 19 has been amended in order to more particularly point out and distinctly claim the subject matter of the invention.

Claim 45: Claim 45 has been amended to correct a typographical error.

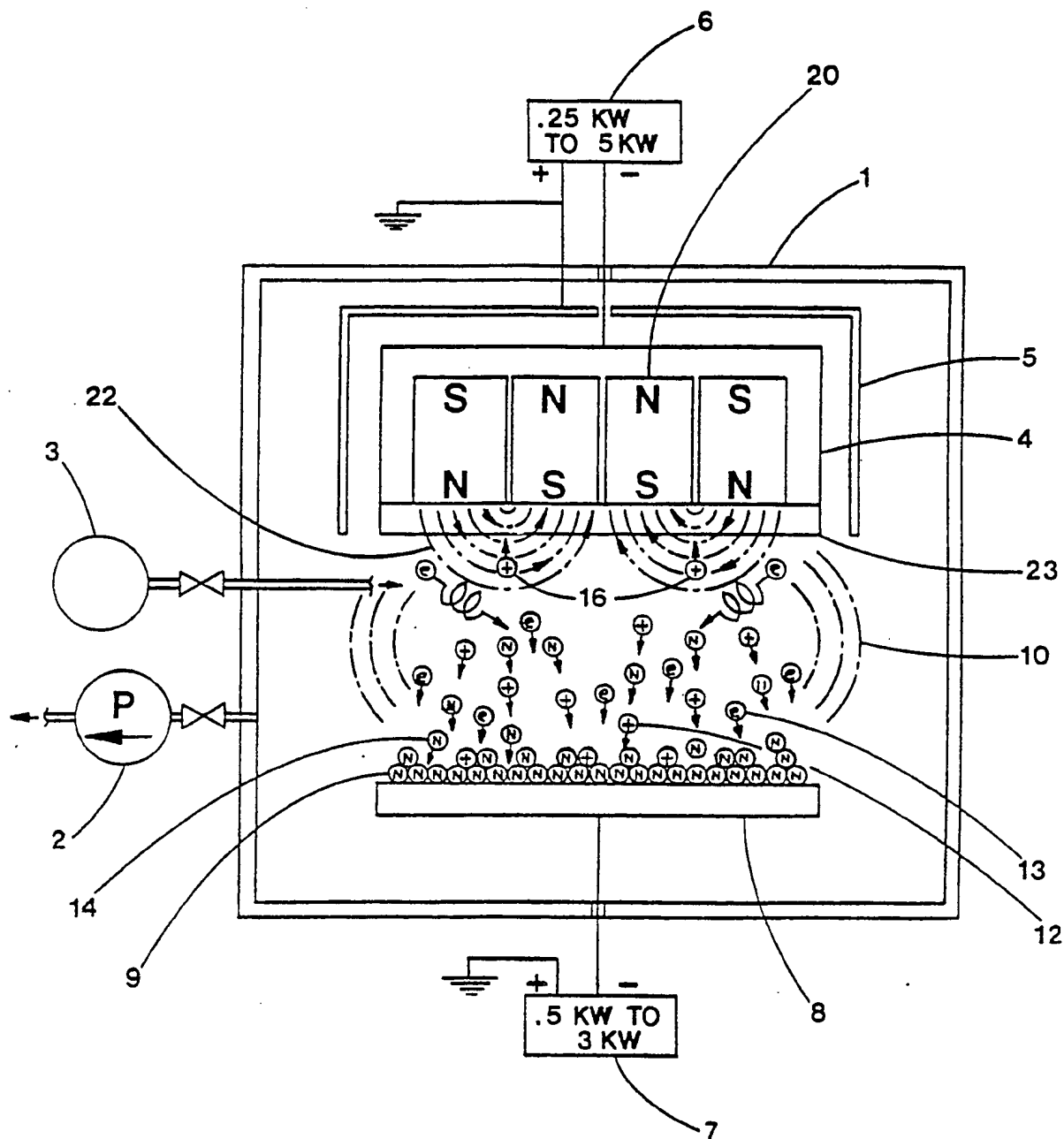
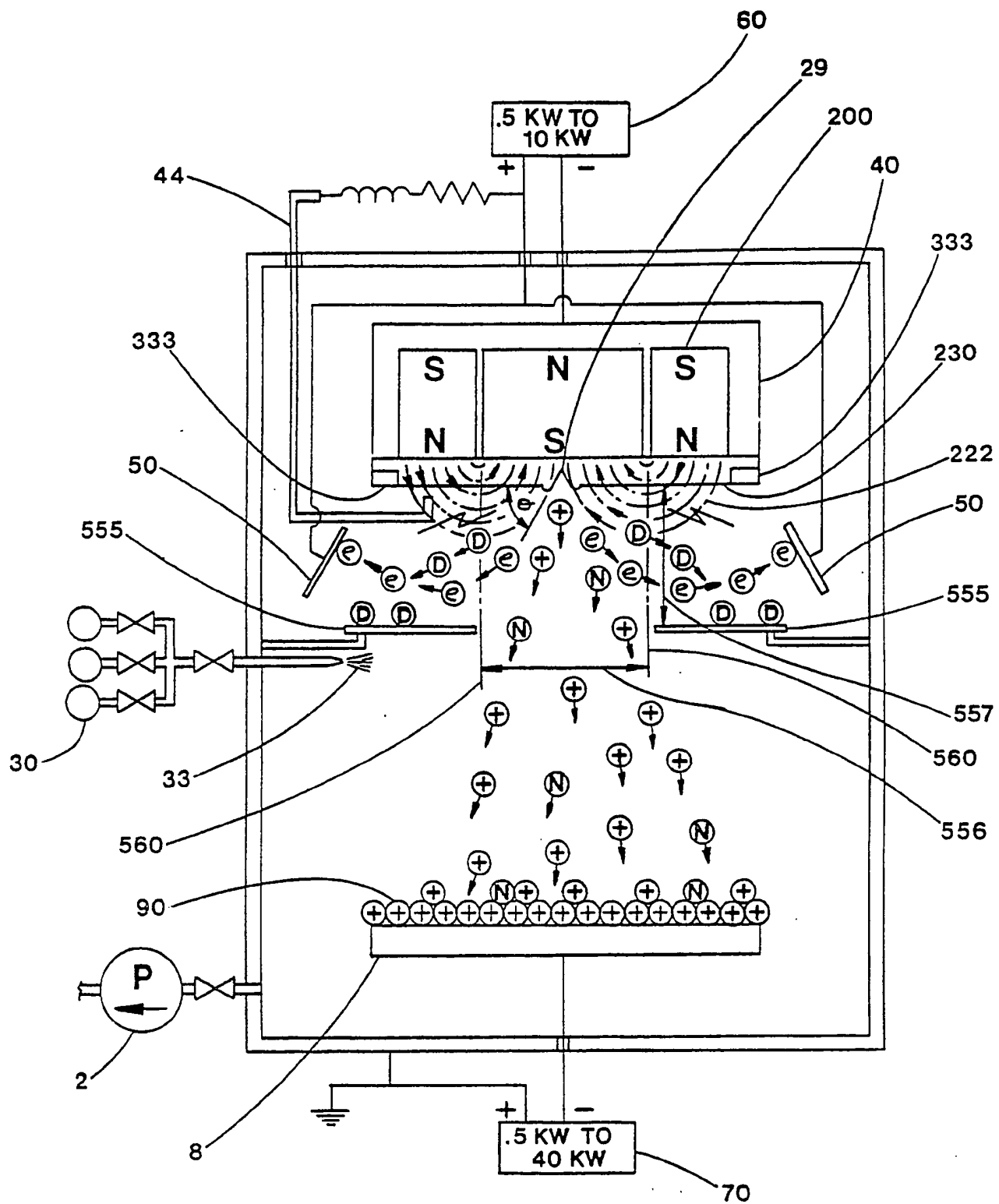


FIG. 1

SUBSTITUTE SHEET

FIG. 2

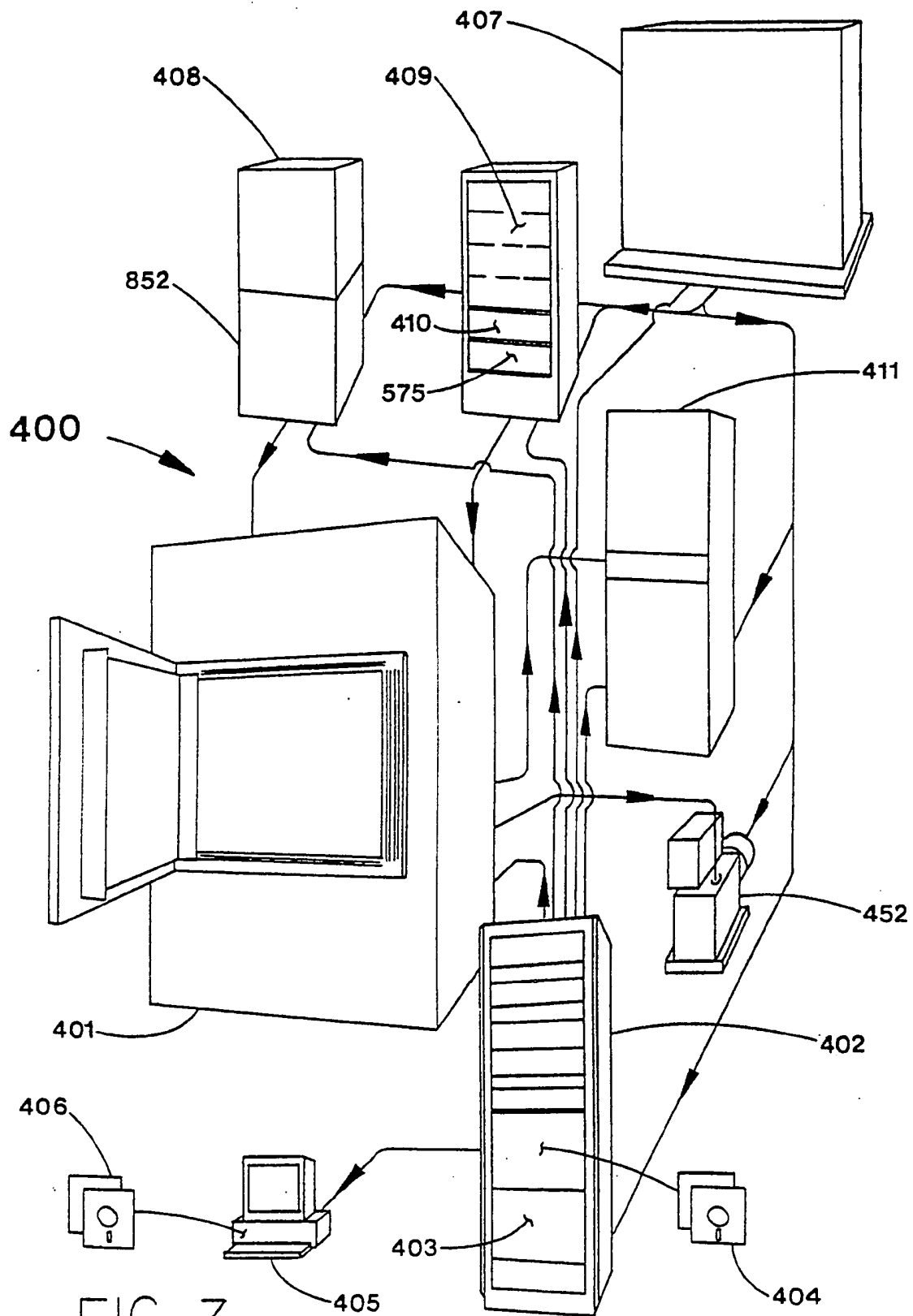
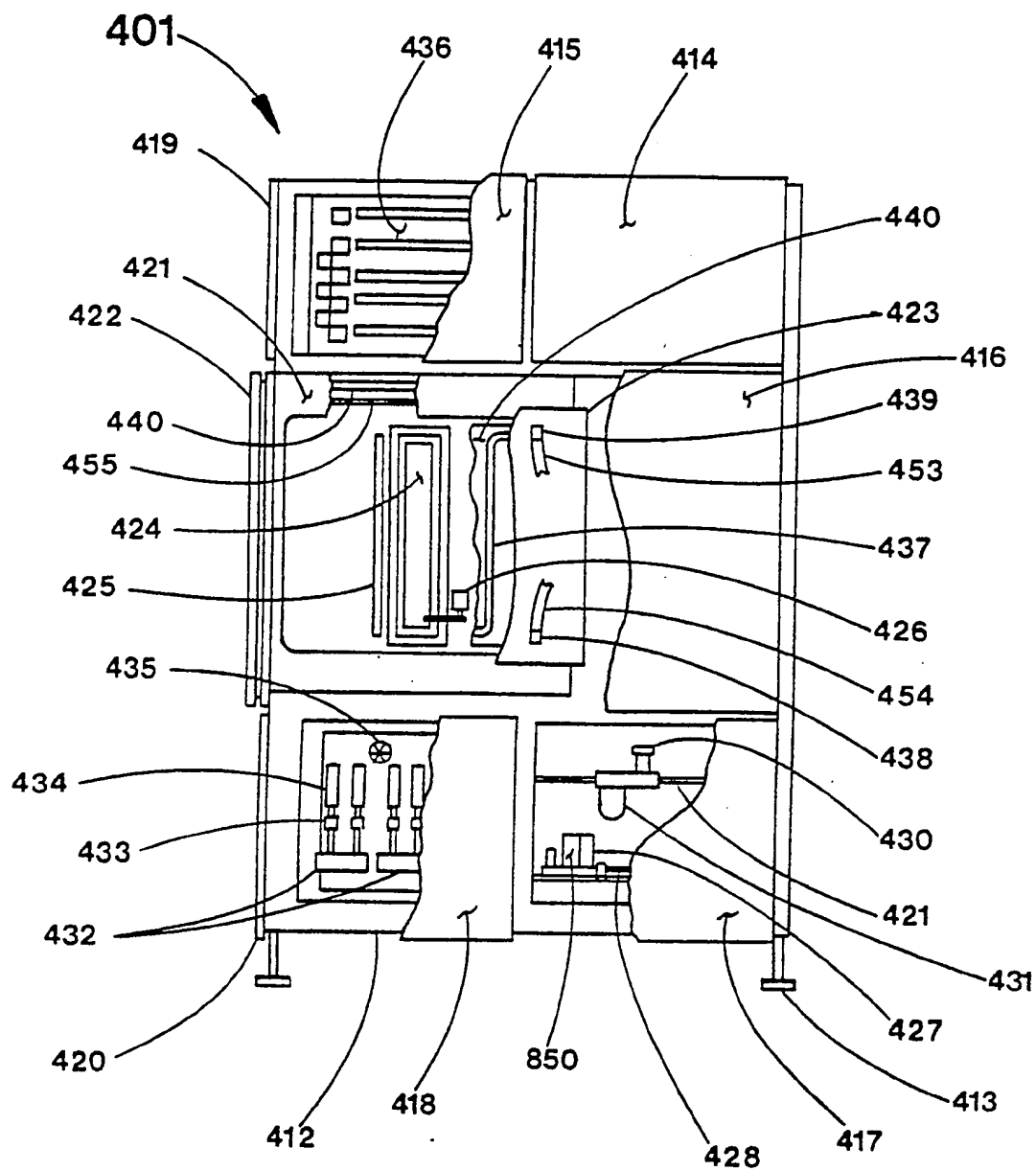
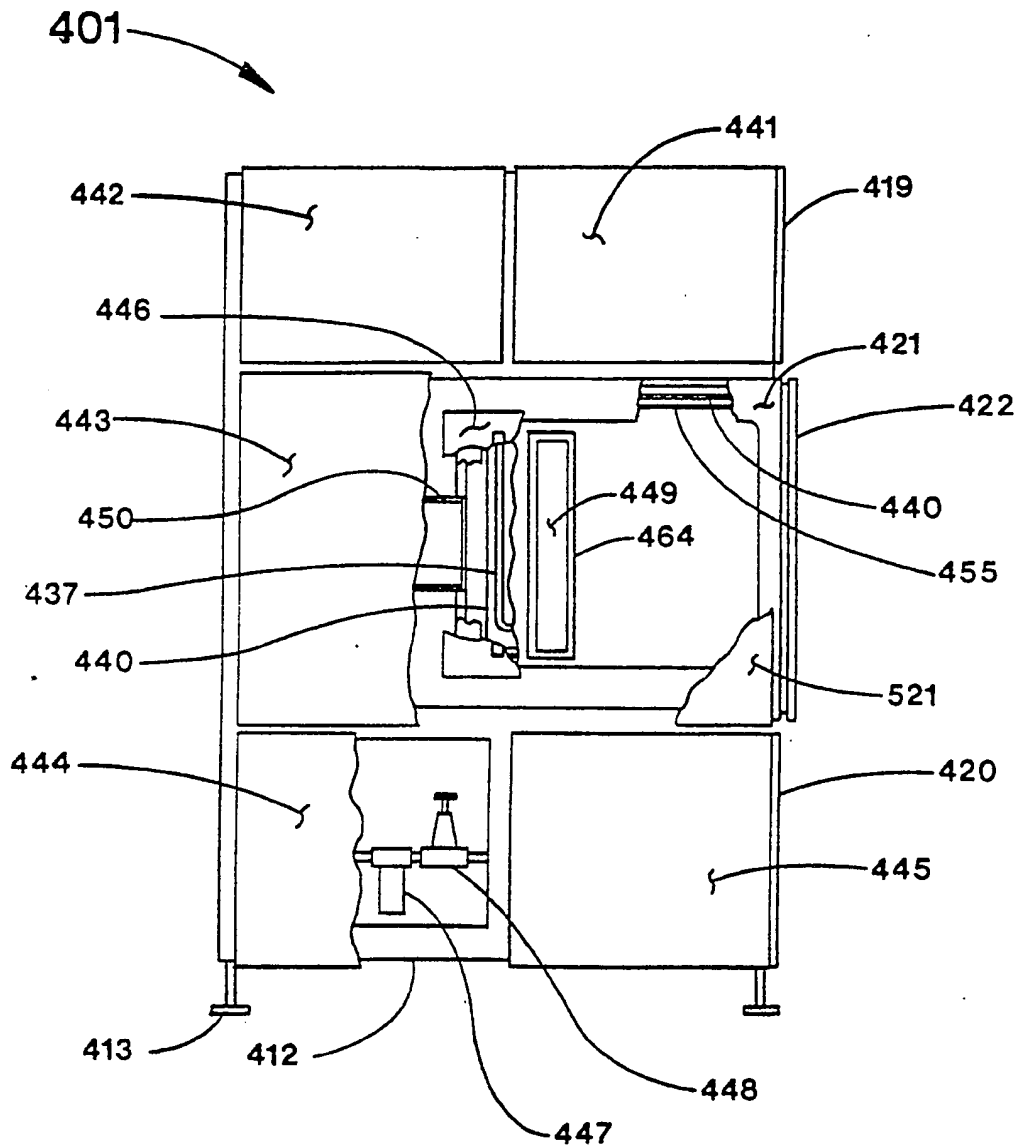
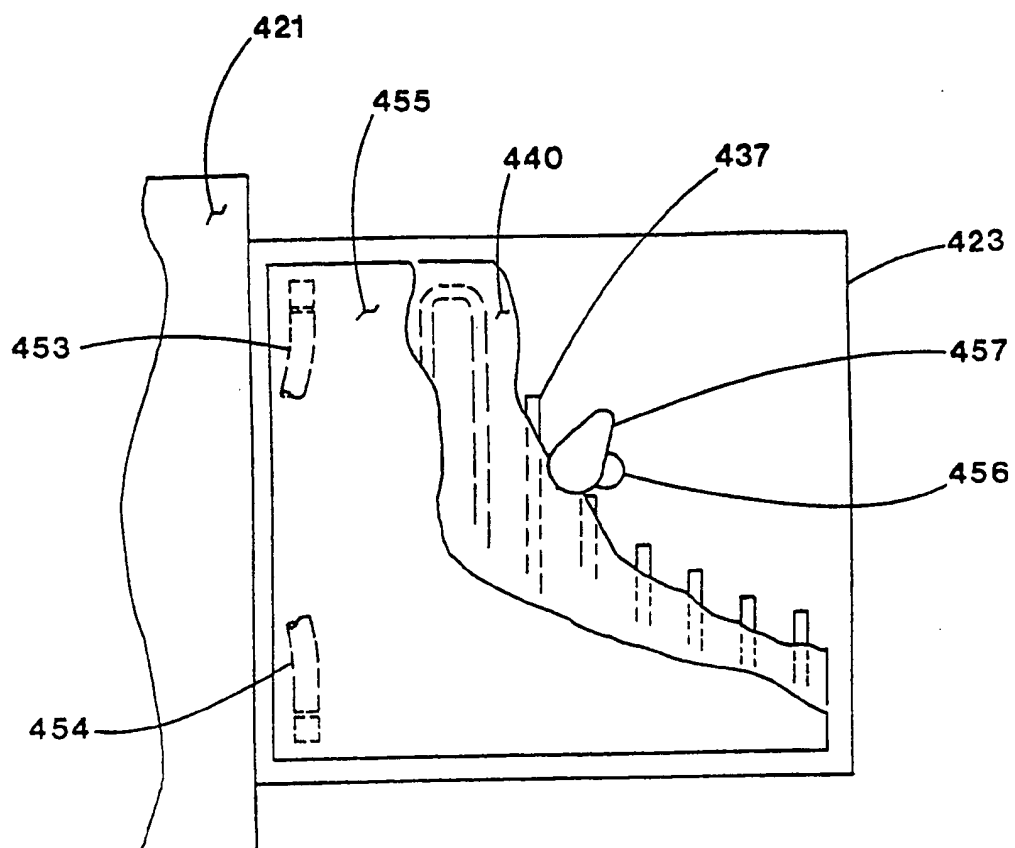
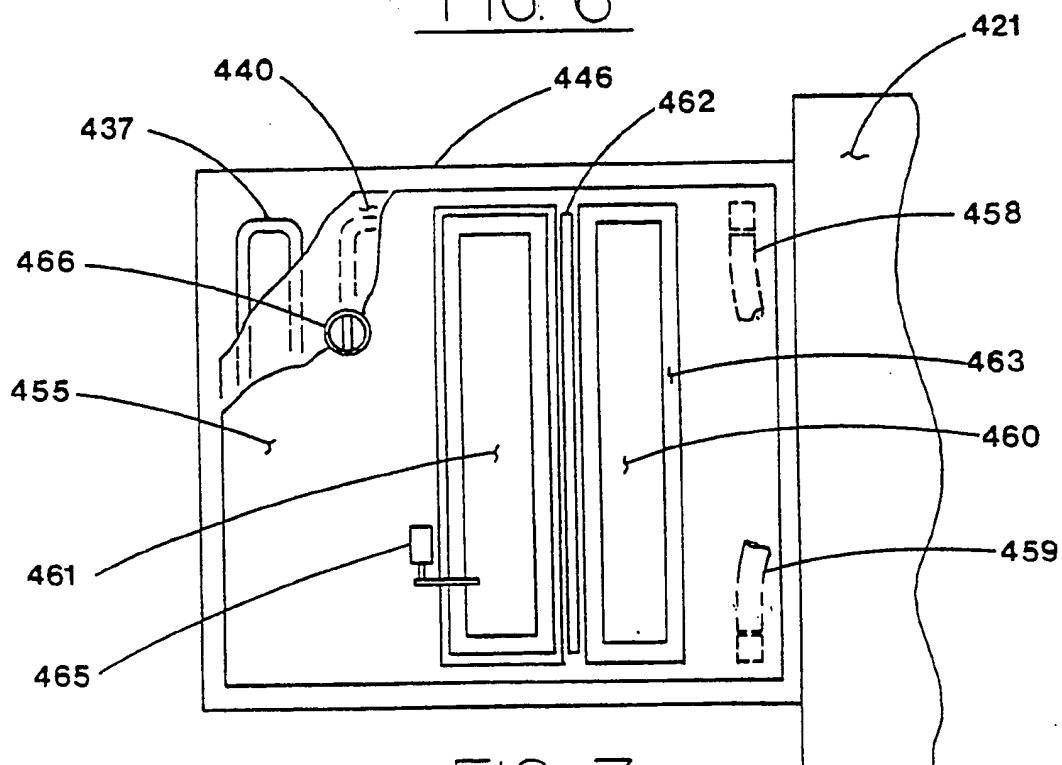
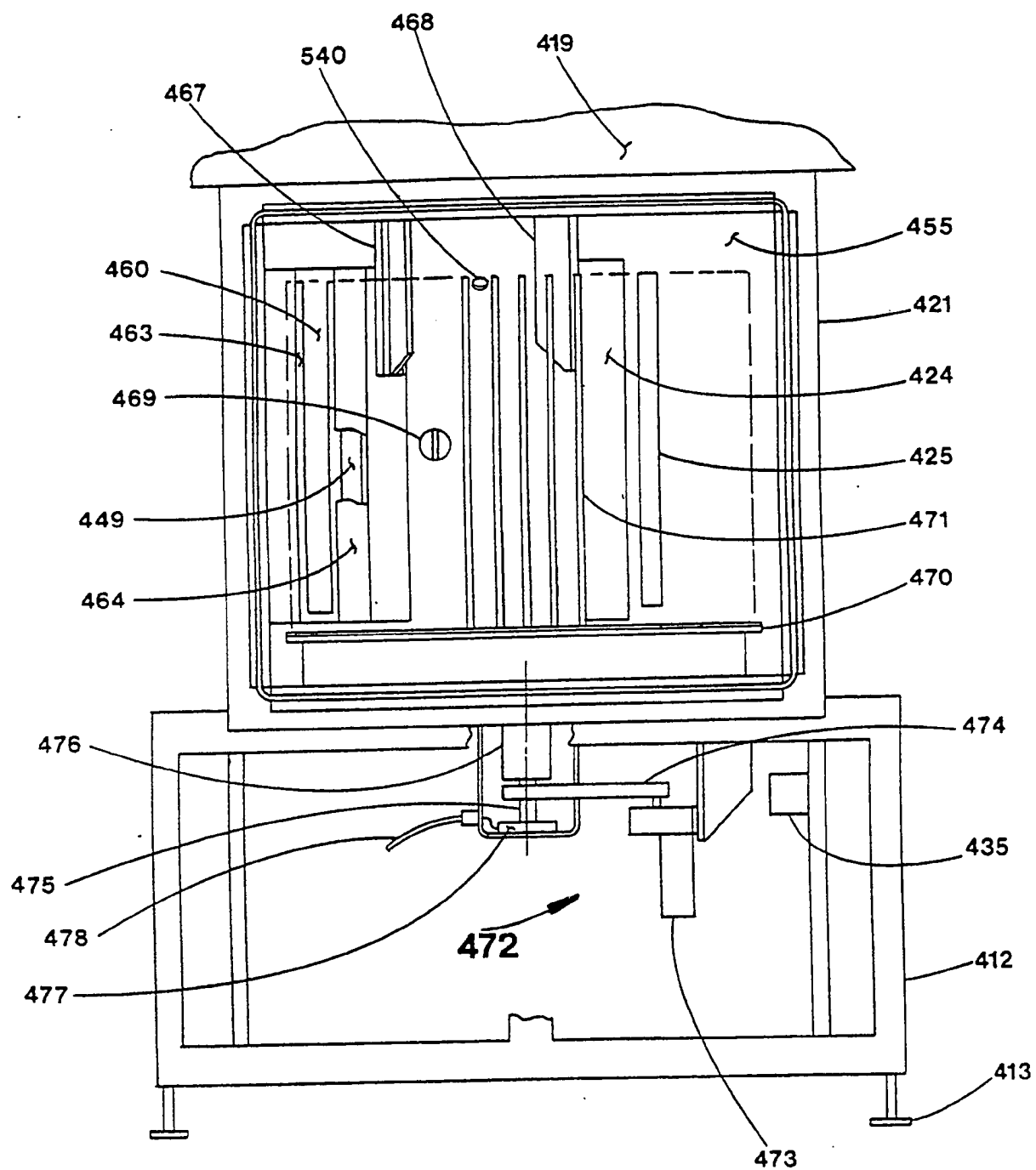


FIG. 3

FIG. 4

FIG. 5

FIG. 6FIG. 7

FIG. 8

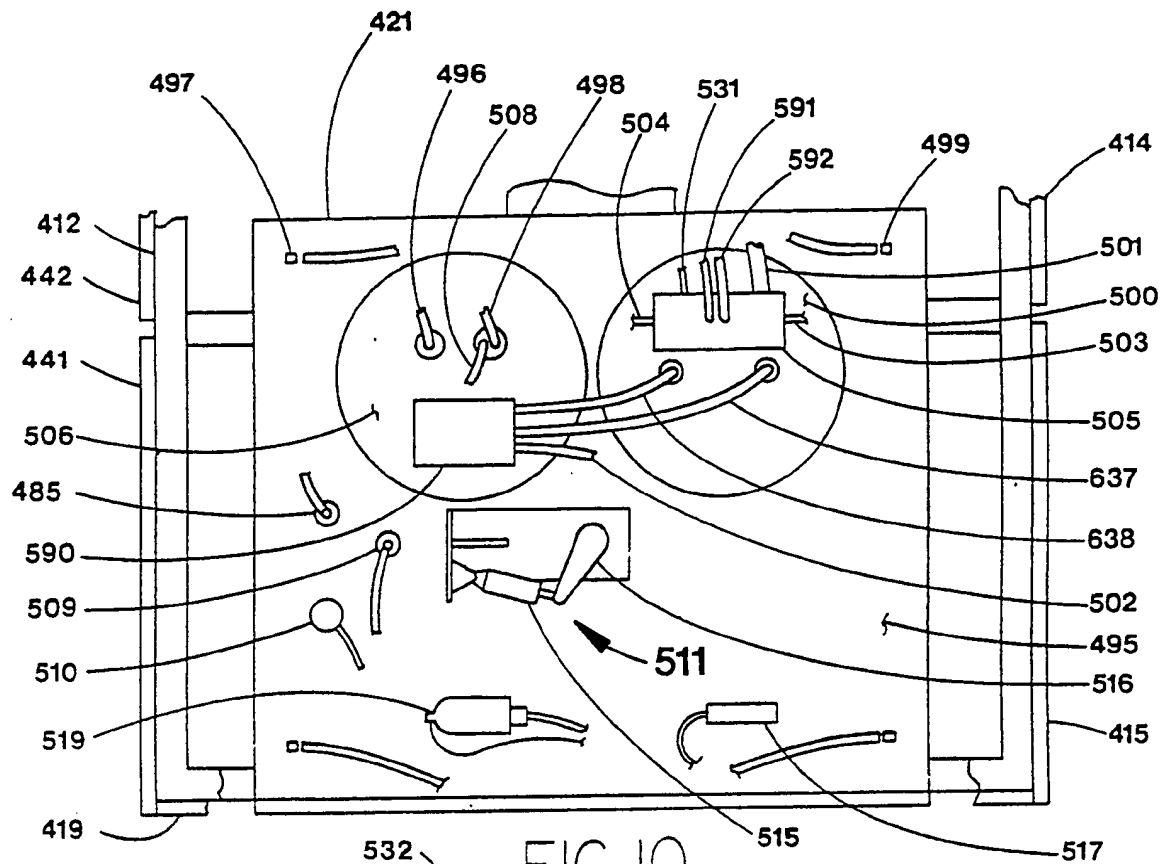


FIG. 10

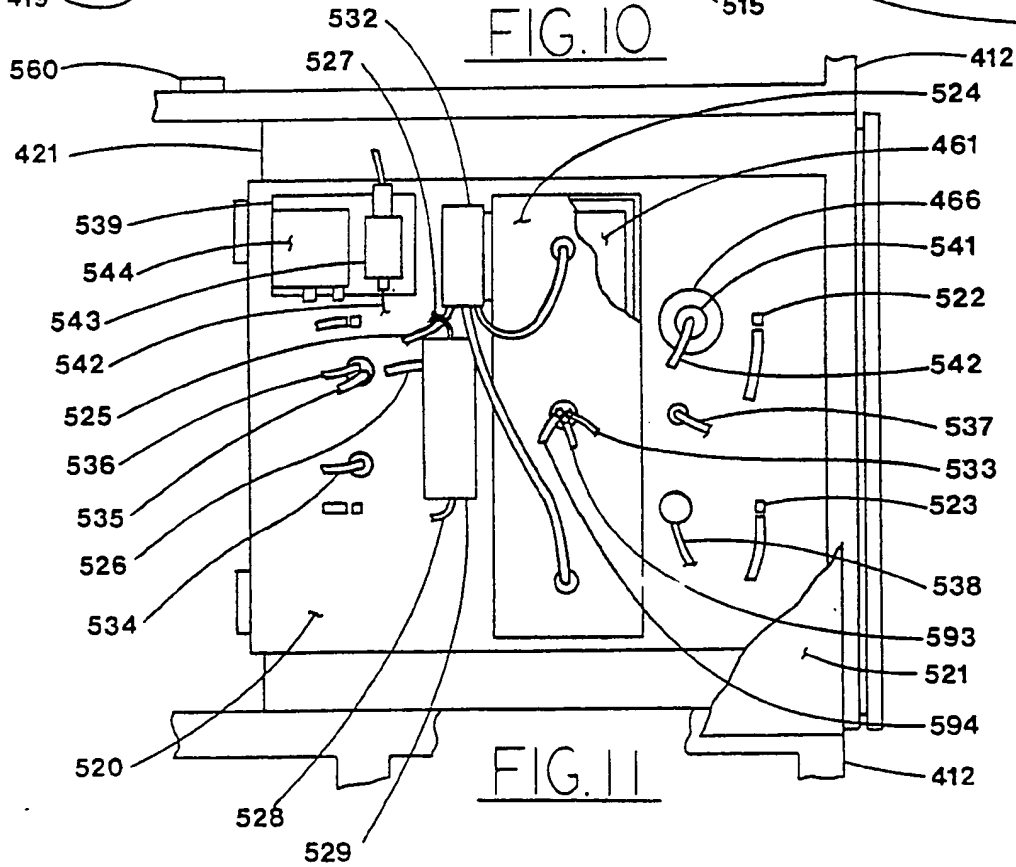
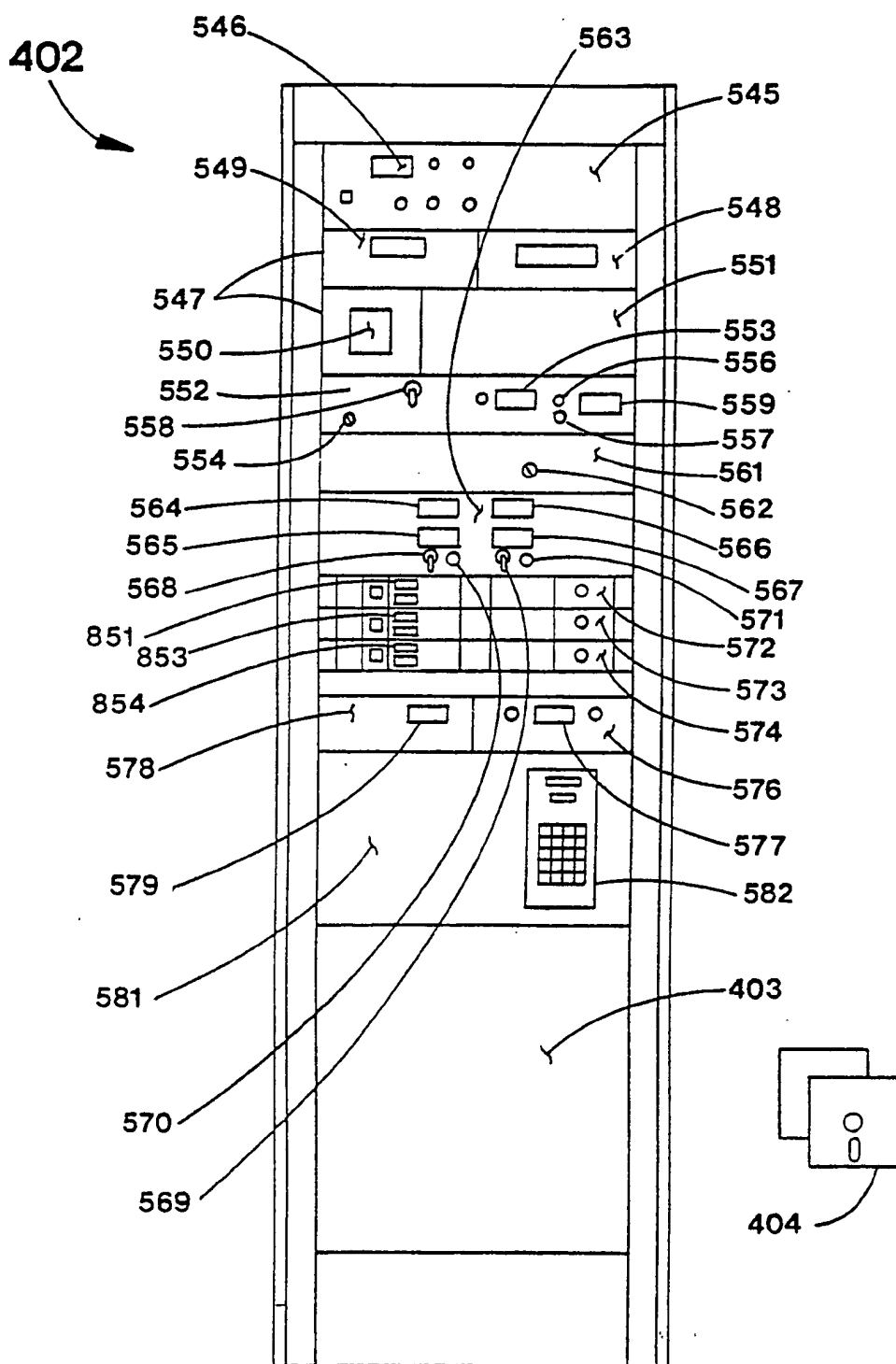
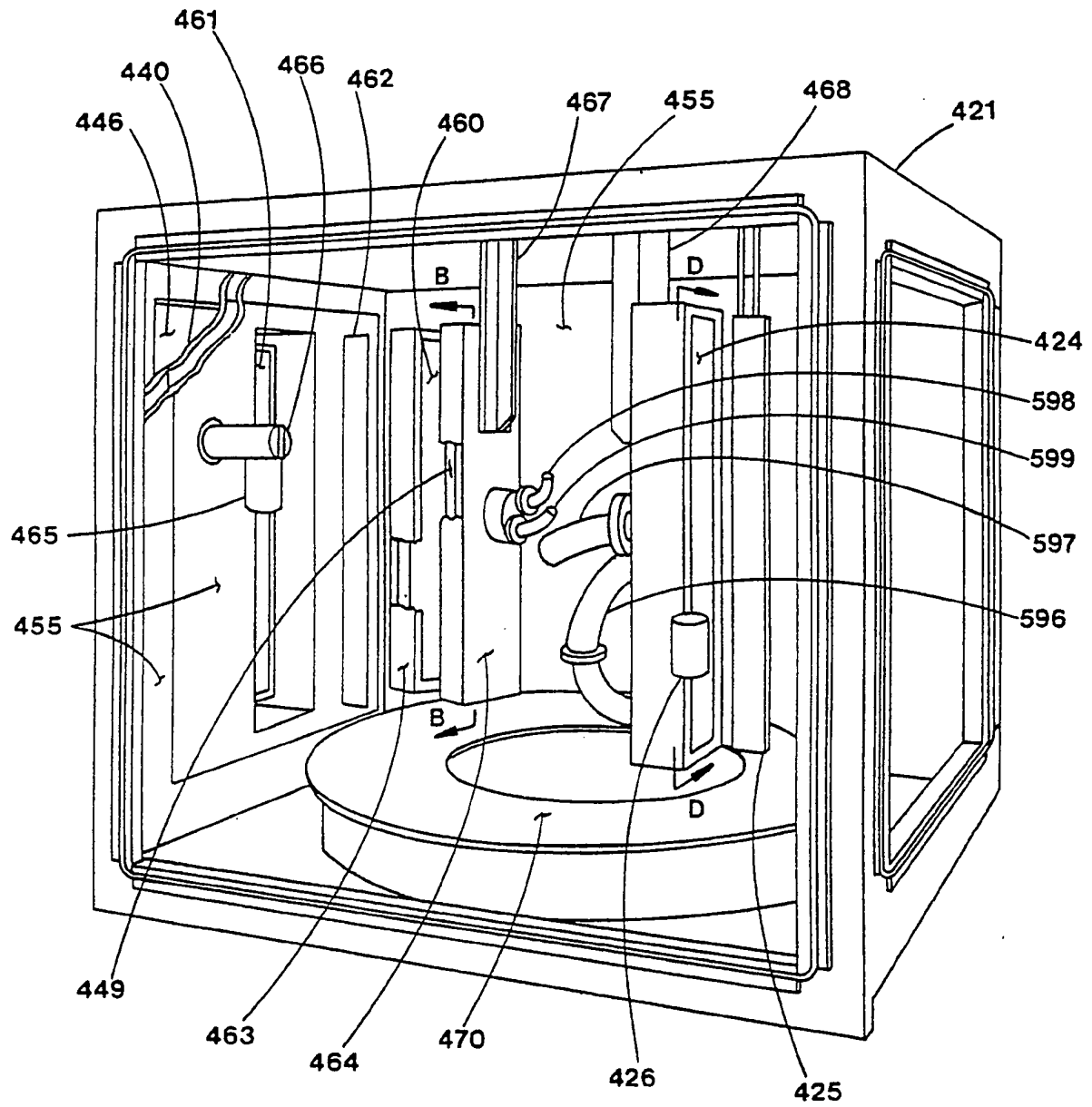
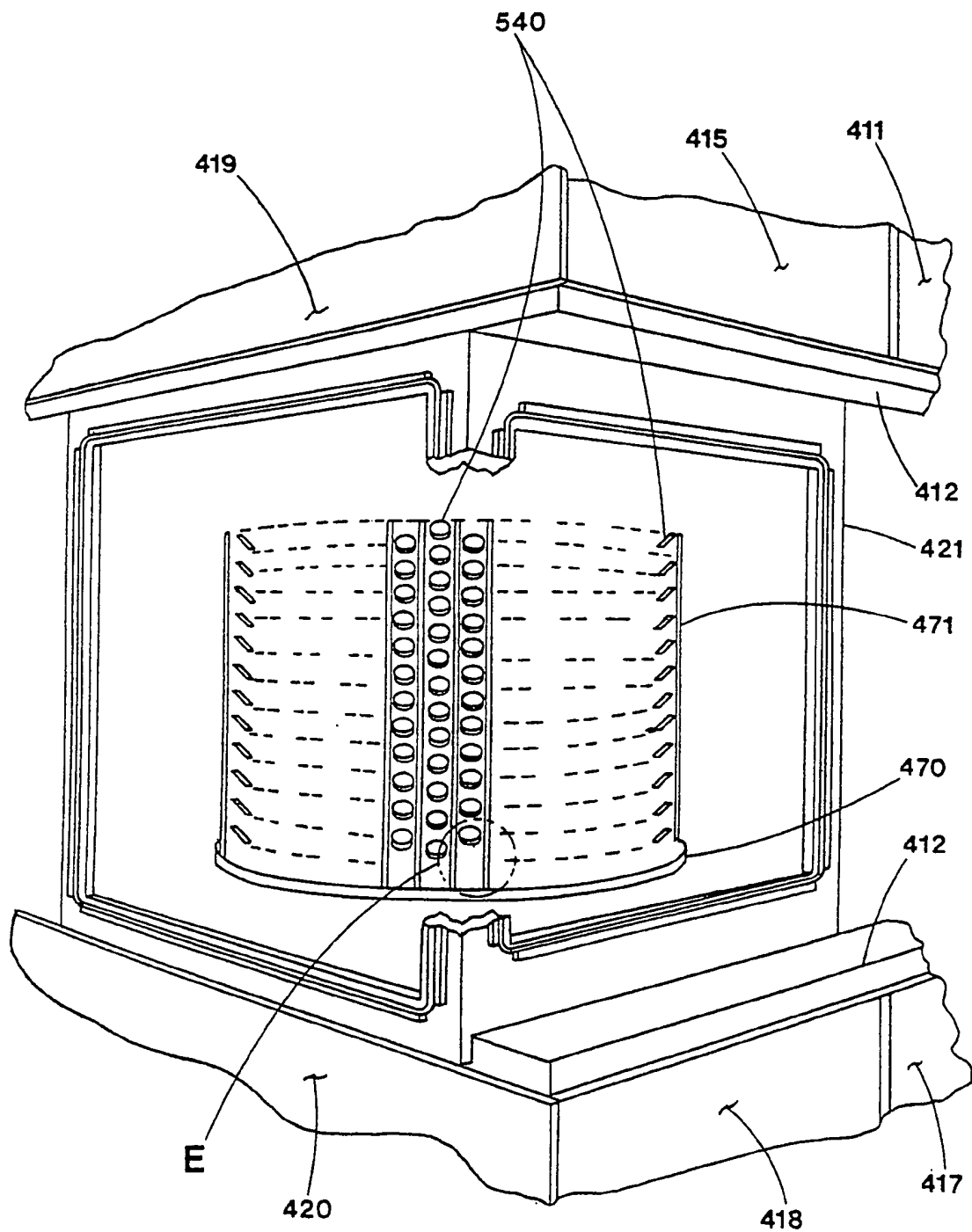


FIG. 11

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FIG. 12

FIG. 13

FIG. 14

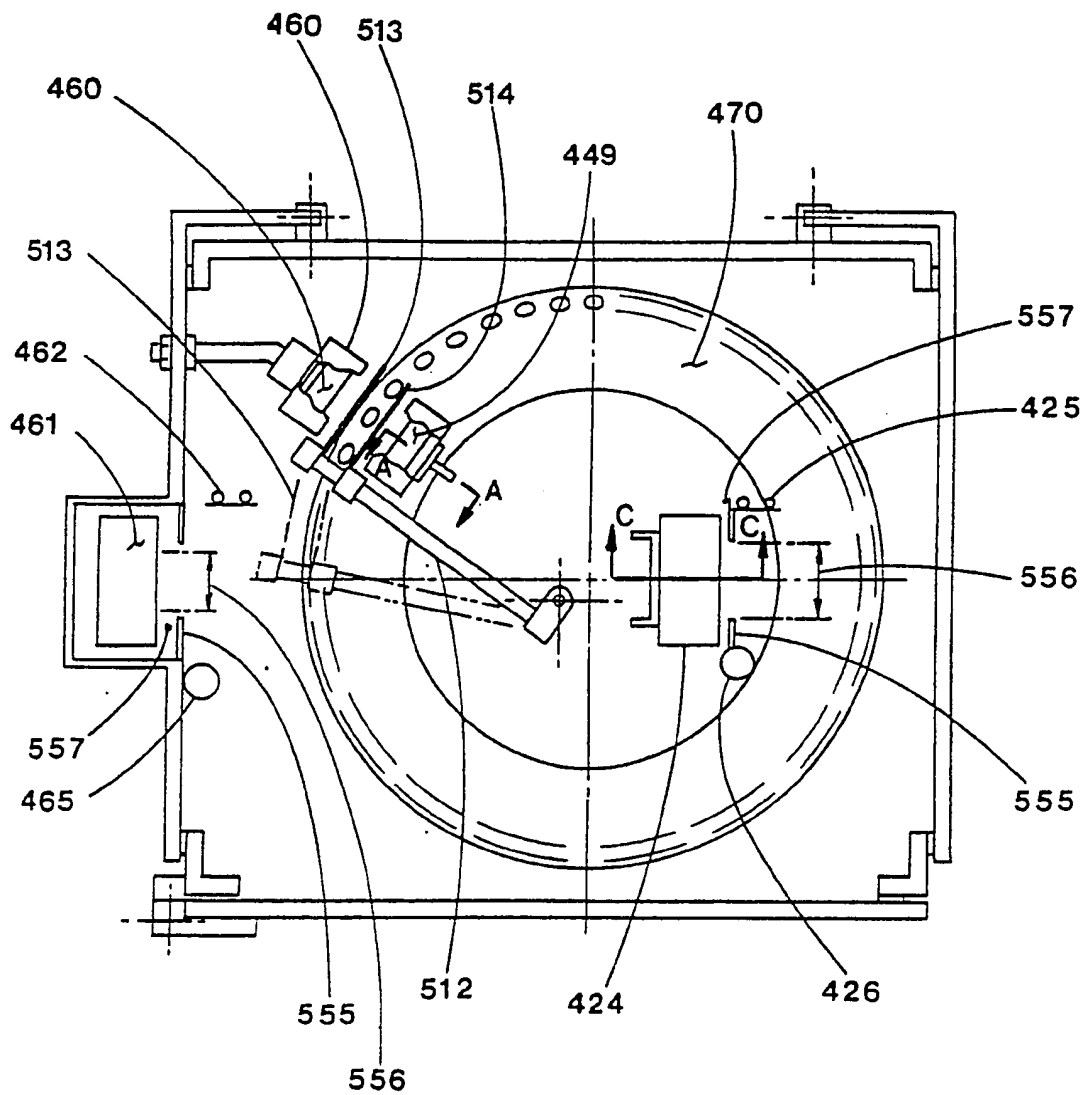


FIG. 15

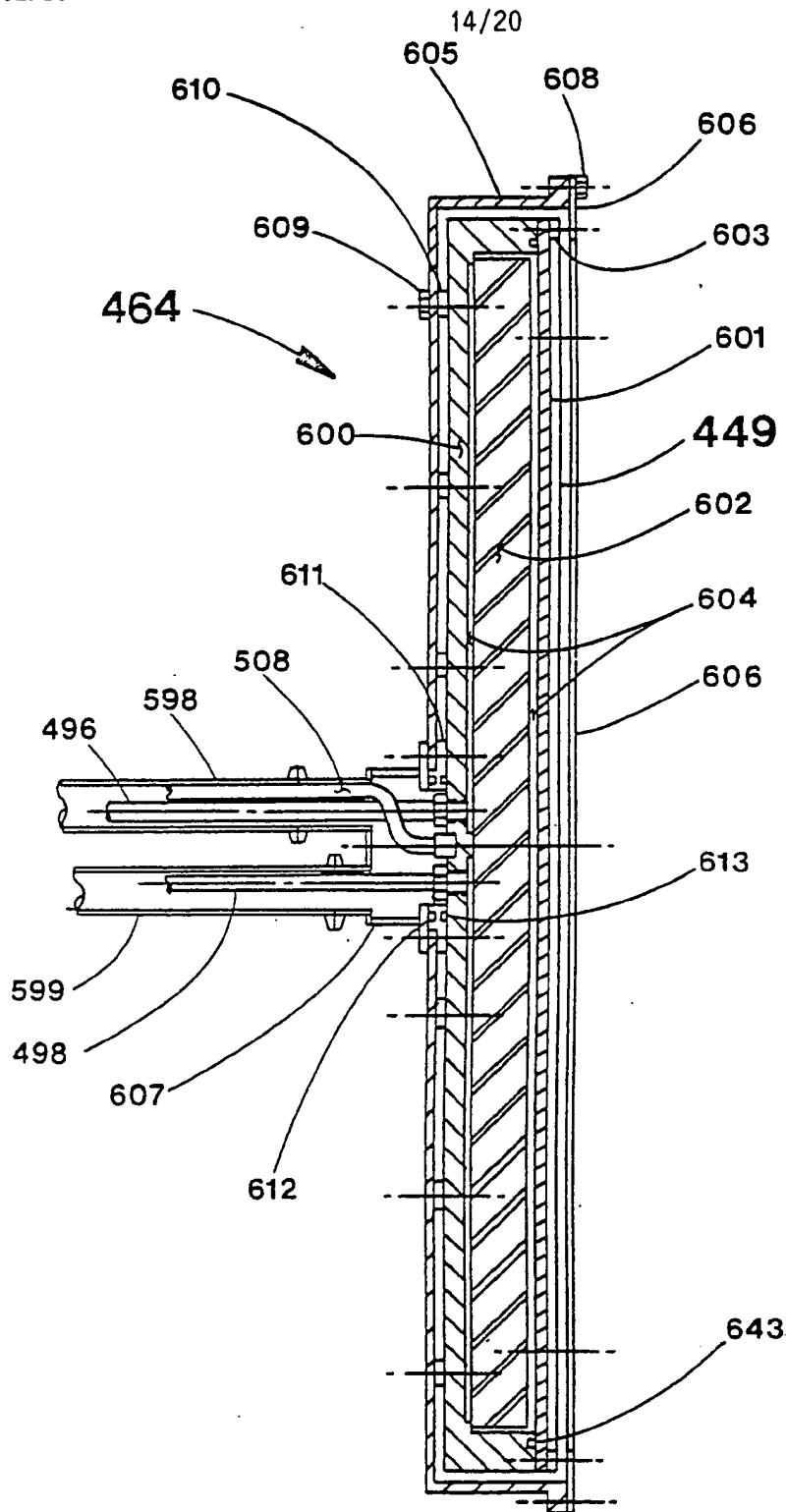
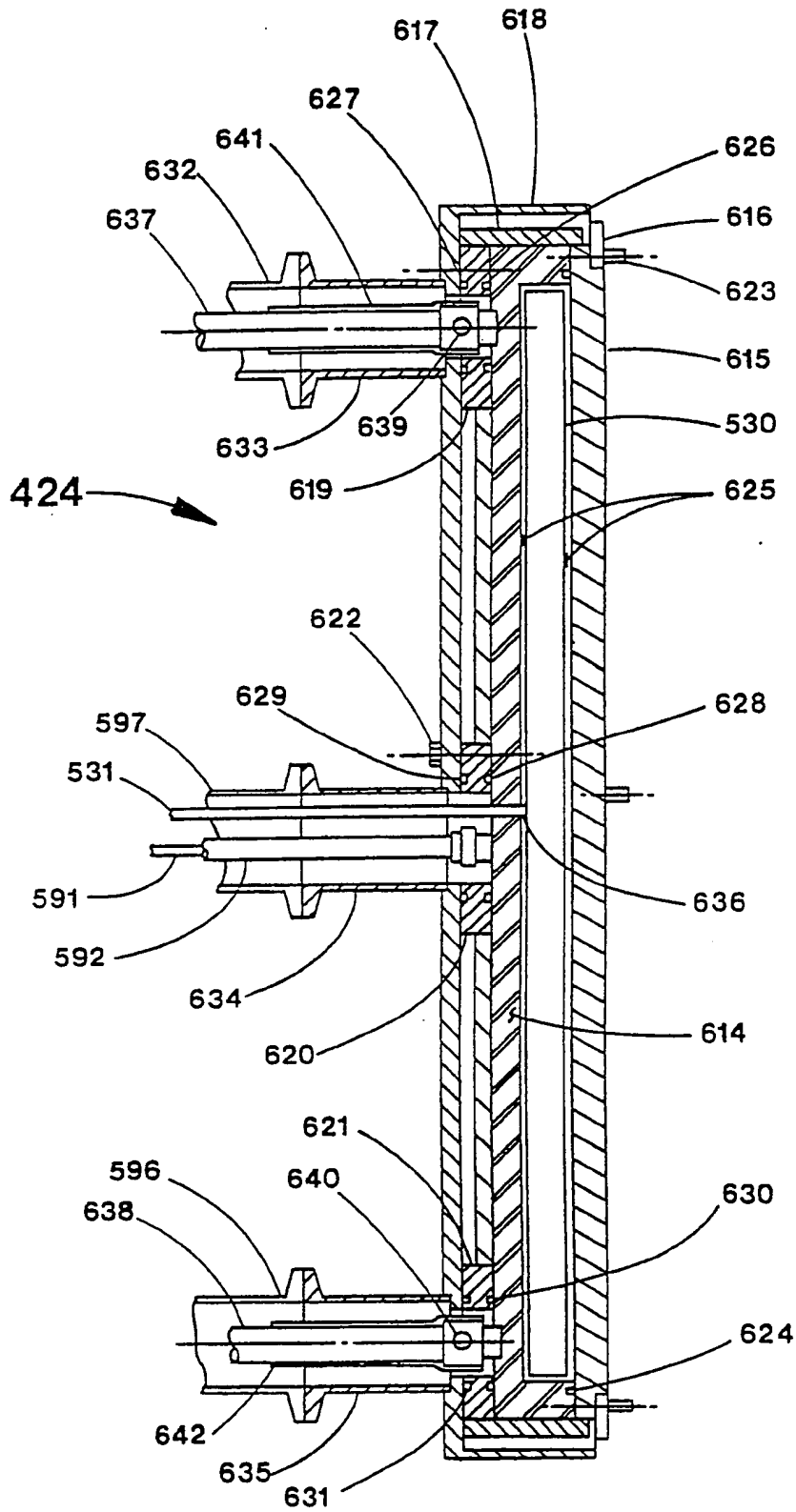
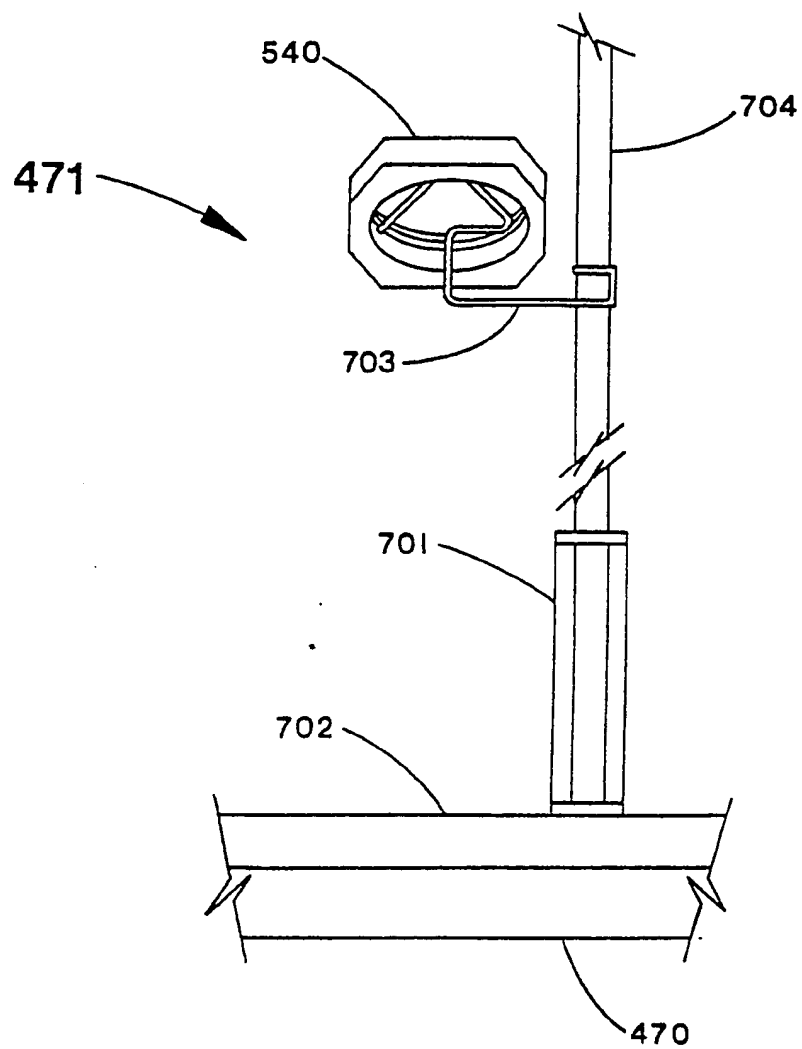
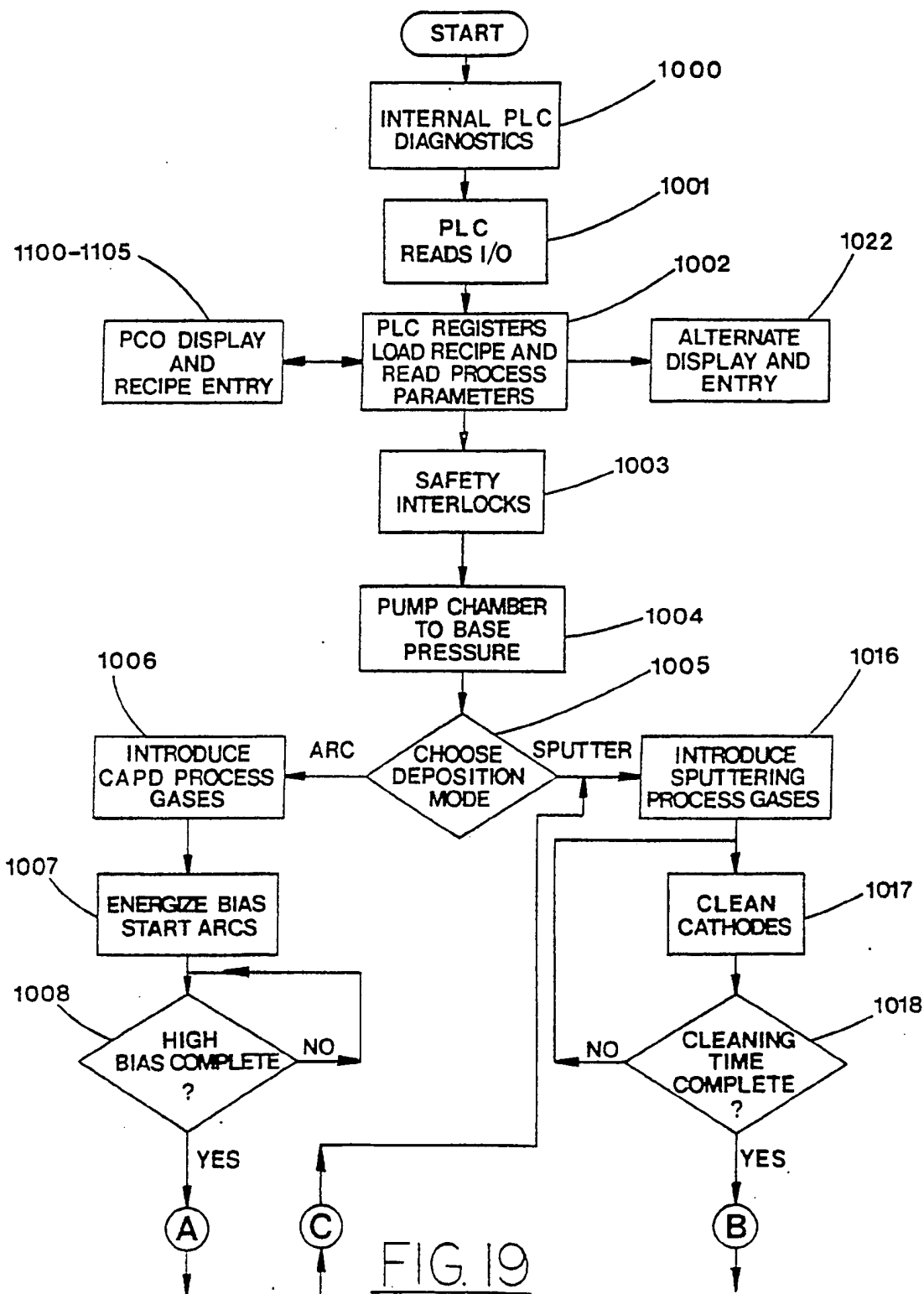


FIG. 16

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FIG. 17

FIG. 18



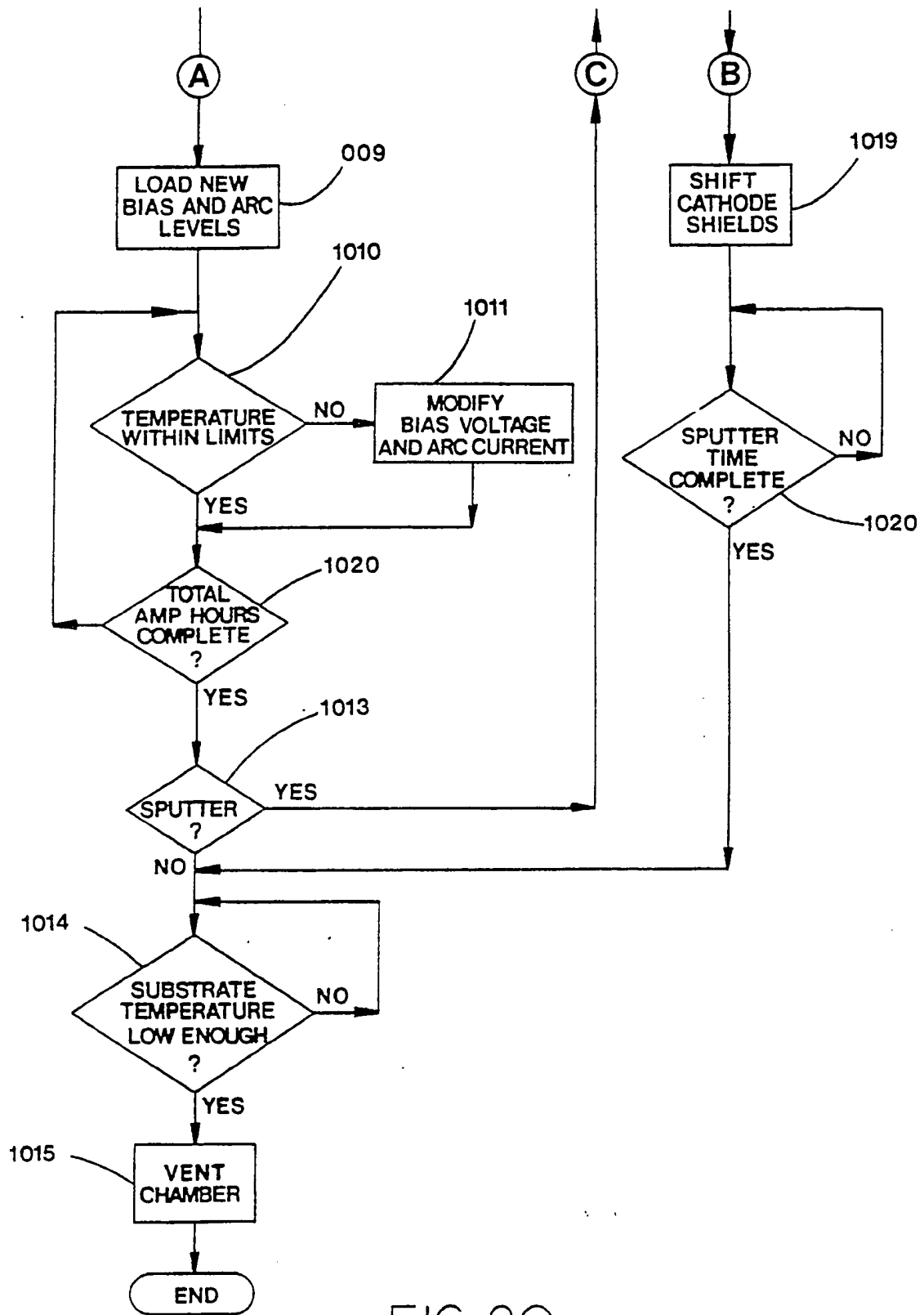
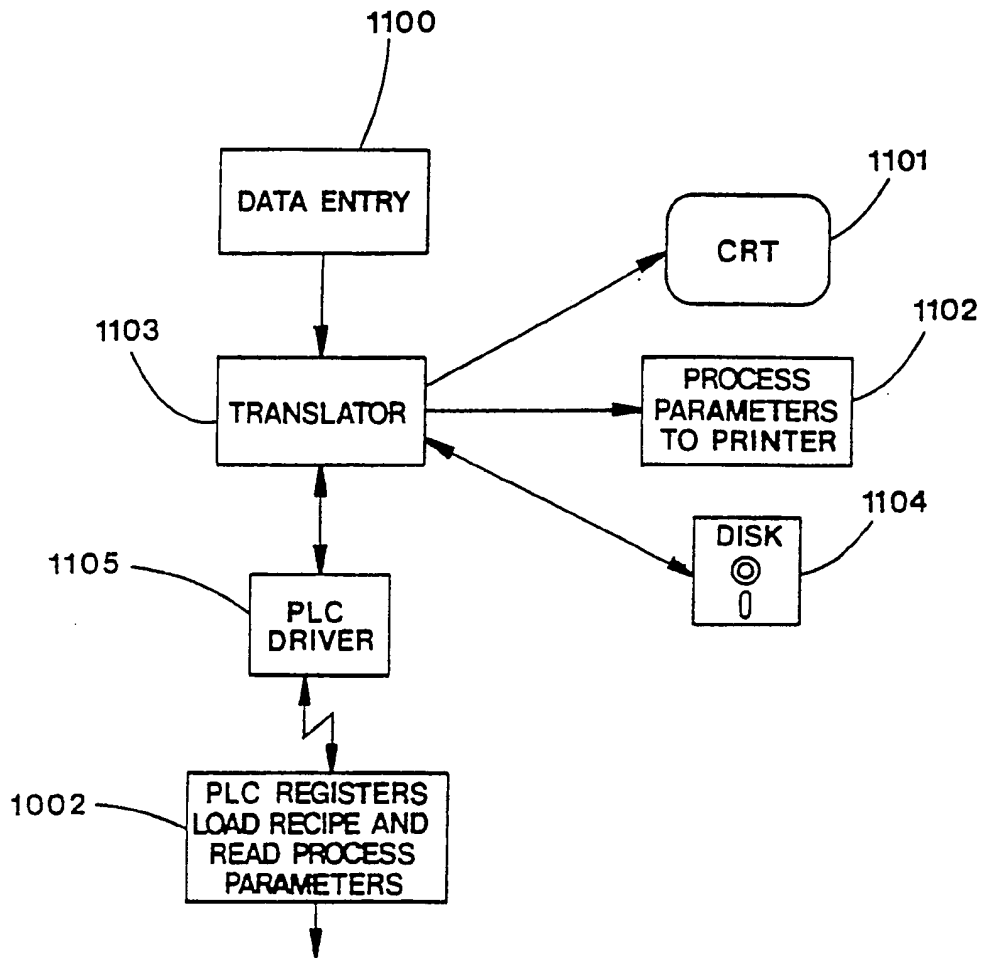


FIG. 20

FIG. 21

S.No.	COMPOSITION	RANGE		
		L'	a'	b'
1	TiN	77-80	2-5	33-37
2	TiC _{0.05} N _{0.95}	76-79	5.5-8	30-33
3	TiC _{0.10} N _{0.90}	71-75	8.5-11	23-28
4	TiC _{0.15} N _{0.85}	66-69	11-16	21-22
5	ZrN	86-89	-3--1	23-25
6	ZrC _{0.10} N _{0.90}	81-84	-1--0.4	26-29
7	ZrC _{0.15} N _{0.85}	79-81	0-3	17-19
8	Gold 10K	81-86	-1.6-1	19-30
9	Gold 24K (Pure)	88-91	-3.7-1	27-34

FIG. 22

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/02950

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ C23C 14/34; C23C 14/54		
U.S. CL. 204/192.38, 298; 364/500		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	204/192.12, 192.13, 192.15, 192.16, 192.17, 192.38, 298MT, 298CS, 298MS, 298PM, 298MC, 298MD, 298D 364/500	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4,234,622 (DU BUSKE ET AL) 18 November 1980	1-38, 40-46
A	US, A, 4,560,462 (SNYDER) 27 May 1988	1-38, 40-46
A	US, A, 4,648,952 (HERKLOTZ ET AL) 17 January 1989	1-38, 40-46
A	US, A, 4,500,408 (BOYS ET AL) 19 February 1985	39
<p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the International filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the International filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Δ" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of the International Search Report
April 10, 1989		17 MAY 1989
International Searching Authority		Signature of Authorized Officer
ISA/US		Aaron Weissstuch